Rocky Mountain Conference on Magnetic Resonance

Volume 36 *36th Rocky Mountain Conference on Analytical Chemistry*

Article 1

July 1994

36th Rocky Mountain Conference on Analytical Chemistry

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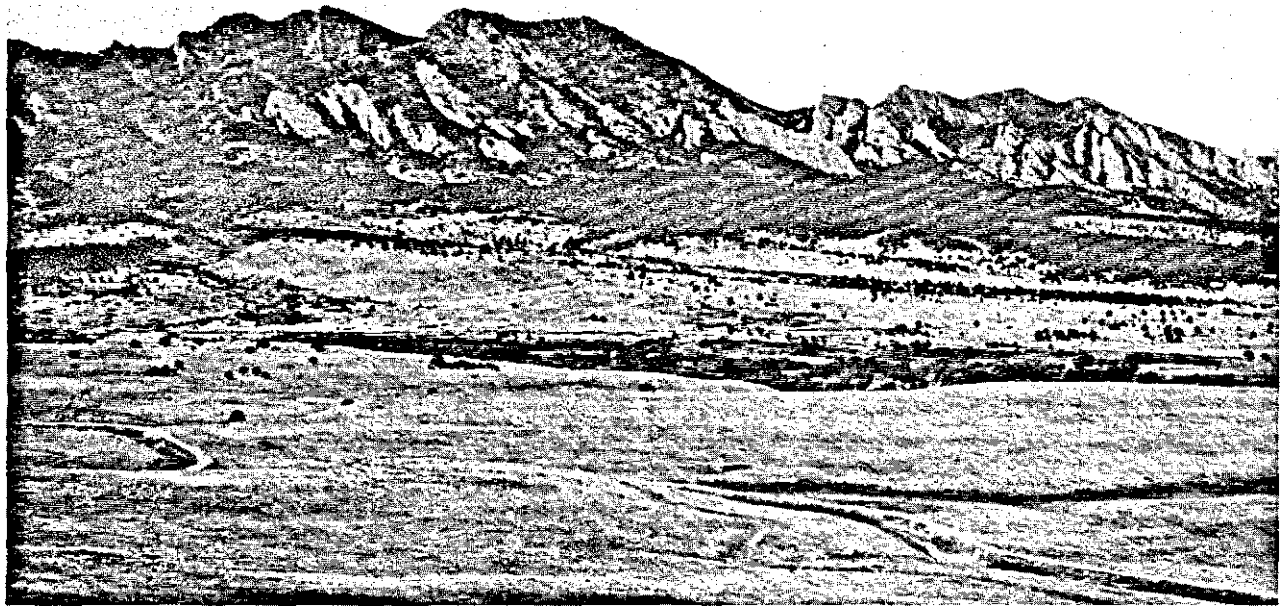

PROGRAM AND ABSTRACTS

JULY 31 - August 5,1994

HYATT REGENCY DENVER
1750 WELTON STREET
DENVER, COLORADO

SPONSORED BY
ROCKY MOUNTAIN SECTION
SOCIETY FOR APPLIED SPECTROSCOPY
&
COLORADO SECTION
AMERICAN CHEMICAL SOCIETY

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VENDOR WORKSHOP SCHEDULE

ROOM	7/31/94 SUNDAY AM	7/31/94 SUNDAY PM	8/03/94 WEDNESDAY AM	8/03/94 WEDNESDAY PM	8/04/94 THURSDAY AM	8/04/94 THURSDAY PM
FLORENTINE	Bruker^ Instruments	Bruker Instruments				
ROYAL	Buck/Western	Buck/Western		CEM	Waters	Waters
PARISIENNE		Varian				
FAR EAST				Dionex	TJA	TJA

Room locations can be found on back of program cover.

SYMPOSIA SCHEDULE

ROOM	8/01/94 MONDAY AM	8/01/94 MONDAY PM	8/02/94 TUESDAY AM	8/02/94 TUESDAY PM	8/03/94 WEDNESDAY AM	8/03/94 WEDNESDAY PM	8/04/94 THURSDAY AM
GRAND BALLROOM	EPR	EPR	EPR	EPR	EPR	EPR	EPR
MOULIN ROUGE	NMR	NMR	NMR	NMR	NMR	NMR	NMR
FAR EAST	ATOMIC ICP/MS	ATOMIC ICP/MS	ENV CHEM	ENV CHEM	ENV CHEM		
PAVILLION	LUMINESC	LUMINESC	LUMINESC				
ROYAL	COMPOST	COMPOST	COMPOST	COMPOST	COMPOST		
GOLD	SPEAKER PREP	SPEAKER PREP	SPEAKER PREP	SPEAKER PREP	SPEAKER PREP	SPEAKER PREP	SPEAKER PREP
FLORENTINE	RADIOCHEM	RADIOCHEM	RADIOCHEM	RADIOCHEM	RADIOCHEM	COMPOST INTERNET	
PARISIENNE	MASS SPEC	MASS SPEC	ELECTRO-CHEMISTRY	ELECTRO-CHEMISTRY		QA	
VISTA	FTIR/NIR	FTIR/NIR	PHARM	PHARM	CHROM	ROBOTICS	
BOARD ROOM	EPR POSTERS	EPR POSTERS	EPR POSTERS	EPR POSTERS	EPR POSTERS	EPR POSTERS	EPR POSTERS
IMPERIAL BALLROOM	EXHIBITS	EXHIBITS	EXHIBITS	EXHIBITS	EXHIBITS	EXHIBITS	
IMPERIAL FOYER	GENERAL POSTERS	GENERAL POSTERS	GENERAL POSTERS	GENERAL POSTERS	GENERAL POSTERS	GENERAL POSTERS	vjrvr^

Organizers of the 36th Rocky Mountain Conference on Analytical Chemistry

Conference Chair- Christine White, Coors Brewing Company, CC284, Golden, CO 80401 (303) 277-2931; fax: 277-6573

Program Chair - Jeff Cornell, Quanterra, Inc., 4955 Yarrow Street, Arvada, CO 80002, (303) 421-6611; fax: 431-7171

Exhibits and Vendor Workshop co-Chairs • Vanessa Fishback, University of Colorado at Denver, Department of Chemistry, Campus Box 194, P.O. Box 173364, Denver, CO 80217-3364, (303) 556-3201; fax: 556-4822

SueZeller, Huffman Laboratories, Inc., 4630 Indiana Street, Golden, CO 80403, (303) 278-4455; fax: 278-7012

Registration Chair - Barbara Coles, Hauser Chemical Research Inc., 5555 Airport Blvd., Boulder, CO 80301, (303) 443-4662; fax: 441-5803

Publicity Chair - Pat Sulik, Rocky Mountain Instrumental Labs, 456 S. Link Lane, Ft. Collins, CO 80524, (303) 530-1169; fax: 530-1169

Treasurer - Glenda Brown, U.S. Geological Survey, MS407, 5293 Ward Road, Arvada, CO 80002, (303) 467-8122; fax: 431-8331

Mailing List - Carol Gies, *EG&G Rocky Flats, General Lab Bldg 881, P.O. Box 464, Golden, CO 80402-0464,* (303) 966-7380; fax: 966-4365

Audio Visual Chair - Ted Struzeski, U.S. Geological Survey, 5293 Ward Road, Arvada, CO 80002, (303) 467-8147; fax: 431-8331

Social Chair - Chuck Bates, Geneva Pharmaceuticals Inc., 2555 West Midway Blvd.,Box 446, Broomfield, CO 80038-0446, (303) 438-4469; fax: 466-7935

Special thanks to Aidan Ridley for being the "honorary Conference Committee Chef"

SYMPOSIA ORGANIZERS

ATOMIC SPECTROSCOPY

Gary Rayson
New Mexico State University
Chemistry Department
Las Cruces, NM 88003
(505) 646-5839
Fax#: (505) 646-2649

CHROMATOGRAPHY

Denise Kent
11671 Baca Road
Conifer, CO 80433
1-800-632-2708 ext. 2168

COMPOSTING

Cal Kuska
8547 E. Arapahoe Rd.
J221
Greenwood Village, CO 80112
(303) 791-8639
Fax#: (303) 850-0623

Robert Wershaw
U.S. Geological Survey
MS 408, 5293 Ward Road
Arvada, CO 80002
(303) 467-8280
Fax#: (303) 467-8240

ELECTROCHEMISTRY

Carl Koval
Department of Chemistry Box 215
University of Colorado
Boulder, CO 80309-0215
(303) 492-5564
Fax#: (303) 492-5894

ENVIRONMENTAL CHEMISTRY

Maria Tikkanen
Association of California Water
Agencies
910"K" Street, Suite 250
Sacramento, CA 95814
(916) 441-4545
Fax#: (916) 441-7893

EPR

Gareth Eaton
University of Denver
Chemistry Department
Denver, CO 80208
(303) 871-2980
Fax#: (303) 871-2254

Sandra Eaton
University of Denver
Chemistry Department
Denver, CO 80208
(303) 871-3102
Fax#: (303) 871-2254

FTIR/NIR/RAMAN SPECTROSCOPY

Abdul Chughtai
University of Denver
Chemistry Department
Denver, CO 80208
(303) 871-4404
Fax# (303) 871-2932

GENERAL POSTERS

Mary Cast
QMG National Water Quality Lab
U.S.G.S. 5293 Ward Road
Arvada, CO 80002
(303) 467-8135
Fax#: (303) 467-9598

ICP/MS

Howard E. Taylor
3215 Marine Street
Boulder, CO 80303
(303) 541-3007
Fax#: (303) 447-2505

LUMINESCENCE

DeLyle Eastwood
Lockheed Environmental Systems and Technology Company
980 Kelly Johnson Drive
Las Vegas, NV 89119
(702) 897-3287
Fax#: (702) 897-6641

Robert Hurtubise
University of Wyoming
Department of Chemistry
Box 3838 University Station
Laramie, WY 82071
(307) 766-6241
Fax#: (307) 766-2807

MASS SPECTROMETRY

Joseph Zirrolli
Department of Pediatrics
K923
National Jewish Center
Denver, CO 80206
(303) 398-1853
Fax#: (303) 398-1694

NMR

Robert Botto
Chemistry Division
Argonne National Lab
Argonne, IL 60439
(708) 252-3524
Fax#: (708) 252-9288

PHARMACEUTICAL ANALYSIS

Mike Cutrera
R.P. Scherer Corporation
2725 Scherer Drive
St. Petersburg, FL 22716
(813)572-4000
Fax#: (813) 573-2503

Robert Lantz
Rocky Mountain Instrumental Labs
456 South Link Lane
Fort Collins, CO 80524
(303)530-1169

Patricia Sulik
Rocky Mountain Instrumental Labs
456 South Link Lane
Fort Collins, CO 80524
(303) 530-1169

QUALITY ASSURANCE

William Shampine
U.S.G.S. MS 401
P.O. Box 25046
Denver, CO 80225
(303)236-1940
Fax#: (303) 236-1420

RADIOCHEMISTRY

Ann Mullin
U.S.G.S./NWQL
5293 Ward Road
Arvada, CO 80002
(303) 467-8235
Fax#: (303) 467-8240

ROBOTICS

Jerry Hoffman
U.S.G.S./NWQL
5293 Ward Road
Arvada, CO 80002
(303) 467-8082
Fax#: (303) 467-8240

CONFERENCE LOCATION

Technical sessions and the exhibition for the 36th Rocky Mountain Conference on Analytical Chemistry will be held in the Hyatt Regency Denver, 1750 Welton Street, Denver, Colorado 80202

REGISTRATION

Admission to all technical sessions, vendor sponsored users groups and the exhibition is by the name badge for the 36th Rocky Mountain Conference. Conference fees are payable by check (denominated in $US, only) made payable to the Rocky Mountain Conference.

REGISTRATION FEES -1994

Registration (entire conference and exhibition)	$80.00
Registration (one specified day)	$45.00
Student Registration (requires ID)	$35.00
Student Registration (one specified day)	$15.00
Additional Vendor Registration	$45.00
Unemployed or Retired Registration	$35.00
Exhibition only (non-vendor)	$15.00
Coors Tour (limited to first 75 people)	$15.00

REFUNDS

Requests for refunds of conference fees must be received by July 15, 1994.

REGISTRATION TIMES

On-site registration for the 36th Rocky Mountain Conference will be held in the Imperial Ballroom Foyer of the Hyatt Regency Denver during the following hours:

Sunday, July 31	5:00 p.m. - 9:00 p.m.
Monday, August 1	7:30 a.m. - 3:30 p.m.
Tuesday, August 2	7:30 a.m. - 3:30 p.m.
Wednesday, August 3	7:30 a.m. - 3:30 p.m.
Thursday, August 4	8:00 a.m. - 2:30 p.m.

SPEAKER PREP ROOM

The conference will be providing a speaker prep room this year for your convenience. The Gold Room will have an overhead projector and slide projector available for authors to prepare for their speech if they desire. Please be considerate of others when using the room, as it will be on a first come, first serve basis.

SCHEDULE OF EVENTS

Sunday, July 31	Mixer	7:00 p.m. - 9:00 p.m.
Monday, August 1	Exhibits	9:30 a.m. - 5:00 p.m.
Monday, August 1	Posters	3:00 p.m. - 5:00 p.m.
Monday, August 1	Reception	5:00 p.m. - 8:30 p.m.
Tuesday, August 2	Exhibits	9:30 a.m. - 5:00 p.m.
Tuesday, August 2	Coors Tour	7:00 p.m. 11:00 p.m.
Wednesday, August 3	Exhibits	9:30 a.m. - 5:00 p.m.
Wednesday, August 3	Social Hour	5:00 p.m. - 7:00 p.m.

SOCIAL PROGRAM AT THE HYATT REGENCY DENVER

REGISTRATION NIGHT MIXER

A cash bar will be open in the Imperial Ballroom Foyer of the Hyatt Regency Denver on Sunday evening, July 31, from 7:00 - 9:00 p.m. Plan to meet other conference attendees and beat the Monday rush to pick up your conference badge and abstract book.

GENERAL POSTER SESSION AND CONTEST

This year, the conference is sponsoring a poster contest to acknowledge outstanding submissions in the General Poster session. Since these posters cover a wide range of subjects, they will be judged by attendees on clarity of presentation, display of information, and visual appeal. Come participate in the voting Monday between 3:00 - 5:00 p.m. in the Imperial Ballroom Foyer. Prizes will be awarded for the top three authors.

COORS BREWERY TOUR

Board a double-decker bus for a short ride to historic Golden, Colorado to enjoy a unique tour of the world's largest single-site brewery. Following the tour, light snacks and freshly brewed Coors products and soft drinks will be provided prior to your trip back to the hotel. The tour will be from 7:00 p.m. -11:00 p.m. Tuesday, August 2. Cost for this tour is $15 per person and space is limited to the first 75 people.

WEDNESDAY EVENING SOCIAL HOUR

Join friends and colleagues for a drink at the cash bar in the Imperial Ballroom Foyer from 5:00 - 7:00 p.m. before dinner.

EXHIBITION

The Rocky Mountain Conference exhibition provides an opportunity to see and discuss the latest in analytical instrumentation, supplies, and services. Many vendors will be on hand to display and demonstrate their latest products.

Exhibitors

(as of July 1,1994)

Allen Scientific Glass, Inc.
American Chemical Society, Colorado Section
ATI Instruments, N.A.
Bruker Instruments, Inc.
CEM Corp.
Finnigan Corp.
Fisons Instruments
Hewlett-Packard Co.
High Pressure Diamond Optics
High Purity Standards
Huffman Laboratories, Inc.
Isotec, Inc.
JEOL USA, Inc.
Micro-Now Instrument Co., Inc.
Millipore
Ordela, Inc.
Oxford Instruments Inc.
Oxford Instruments Inc., Nuclear Measurements Division
Perkin Elmer Corp.
Spectra Analytical Instruments, Inc.
SRI Instruments
Star Scientific, Inc.
Summit Scientific
Tecmag, Inc.
Tekmar Co.
Thermo Jarrell Ash Corp.
Varian Associates, Inc.
Waters Chromatography
Webster Scientific
Western Analytical
Wilmad Glass Co.

Rocky Mountain Conference
on
Analytical Chemistry
Exhibition

Invites all conference attendees
to the
Conference Reception
Monday August 1,1994
5-8 pm

Join us in the exhibit area
for

Heavy Hors d'eouvres
Cocktails
Music for your listening pleasure performed by
Blue Heaven

Plus

Open Exhibits
Open Posters with Poster Contest

HOTEL ACCOMMODATIONS

Hotel rooms where the conference is being held, at the Hyatt Regency Denver, 1750 Welton Street, Denver, Colorado 80202, (303) 295-1234, are available at the **special discounted conference rate of $88 per night (single or double), plus applicable tax.** Please identify yourself as a Rocky Mountain Conference attendant when making reservations to receive this discounted rate. A registration form can be located at the back of the preliminary program. Suites are available upon request at the conference discount. The reservation form at the end of the booklet must be returned directly to the hotel. **Conference location and all associated social functions for the conference will be held at the Hyatt Regency Denver.**

VISITOR INFORMATION

Contact the Guest Services in the main lobby of the Hyatt Regency Denver for suggestions on the large number of activities that are enjoyable in Denver and the surrounding area.

MESSAGE CENTER

Incoming telephone messages for conferees will be posted in the Board Room. The telephone number is (303) 295-1234. Indicate the individual is attending the Rocky Mountain Conference so the message can be posted in the proper area.

RESTAURANT SERVICE

The Hyatt Regency Denver Guest Services in the main lobby has sample menus and suggestions for casual to elegant dining experiences throughout the Denver area.

MEMBERSHIP COMMITTEE

Inquiries about membership to the American Chemical Society and Society for Applied Spectroscopy can be addressed to the Colorado Section Membership Committees. Please send inquiries to:

Society for Applied Spectroscopy

Glenda Brown
U.S. Geological Survey
MS407, 5293 Ward Road
Arvada, CO 80002
(303) 467-8122

American Chemical Society

Richard Schwenz, Chairman
University of Northern Colorado
Department of Chemistry
Greeley, Colorado 80639
(303)351-1287

EMPLOYMENT CLEARING HOUSE

The Employment Committee of the Colorado Section of the American Chemical Society will conduct an employment clearing house. Resumes will be accepted prior to, and during the meeting, for review by prospective employers. Employers who are interested in using this employment booth should register by contacting one of the employment committee members listed below by July 15,1994.

Dr. Robert Torres, Chairman
NREL
1617 Cole Boulevard
Golden, CO 80401-3393
(303) 231-1493
FAX (303) 231-1955

Laura Evanson
Schuller International
10100 West Ute Avenue
Littleton, CO 80127
(303) 978-2569

Interested employers and job seekers can receive additional information on available jobs by calling the ACS Employment committee Hotline number which is (303) 933-4375.

SHORT COURSES

Sponsored by the Colorado Section of the ACS
in conjunction with the 36th Rocky Mountain Conference on Analytical Chemistry

Basic Principles of Gas Chromatographv/Mass Spectrometry and Interpretation of Organic Mass Spectra

August 3-5,1994 Fee: $400 member; $450 non-member Faculty: Dr. Joseph Zirrolli

This course will describe the principles of gas chromatography/mass spectrometry and apply them to the identification of organic compounds. Gas chromatography (sample preparation and derivatization, injectors, column selection), ionization processes (positive, negative, chemical, electronic modes), mass analysis and detection will be discussed with emphasis on molecular ion analysis and understanding simple fragmentation processes. The course will develop an approach to the determination of elemental composition and diagnostic fragmentation patterns, and the student will become familiar with mass spectra of pesticides and pollutants. The interpretation approach is based upon, and uses as a reference, the Interpretation of Organic Mass Spectra, Fourth Edition by F.W. McLafferty, and F. Turecek, University Science Books, 1993.

Quality Assurance Practices for the Environmental Laboratory

August 4-5,1994 Fee: $400 member; $450 non-member Faculty: Steve Callio

This course is designed for laboratory analysts, engineers, project managers, and others who require an introduction to quality assurance and quality control practices as applied to environmental measurements. The course will begin with a brief discussion of some basic statistical concepts (i.e. mean, standard deviation, confidence intervals, detection limits, etc.). This is followed by in-depth discussions of the principles and practices of important quality control operations. These range from the preparation of duplicate and spiked sample use of internal standards and standard reference materials to instrument calibration, the role of the QA manager, training requirements and record documentation. The emphasis of this class is on real applications and problem solving.

Laboratory Waste Management

August 4-5,1994 Fee: $550 member; $600 non-member Faculty: Cindy Salisbury and Russell Phifer

If you are a lab manager, researcher, or technician responsible for management of laboratory waste, you should attend this course. Participants will learn which environmental regulations apply to management of your laboratory's waste and how to classify laboratory waste in accordance with RCRA regulations. You will also learn how to manage discarded samples, standards and QA solutions, and the components necessary for an effective laboratory waste management program. You will receive up-to-minute regulatory information and citations. You will learn how to implement a comprehensive environmental compliance program at your laboratory.

Air Toxics Analysis

August 4-5,1994 Fee: $400 member; $450 non-member Faculty: Drs. Larry Anderson and Don Stedtman

This course is designed for laboratory analysts, engineers, project mangers, or others who just want further information about air toxics chemistry, "brown cloud" sampling techniques and analysis, and standard EPA analysis methodologies. The course will present basic air pollution chemistry, State and Federal programs that require air toxics characterization, modern air pollution sampling techniques such as passive and active sampling devices, denuders, and cryogenic preconcentration. The last day will concentrate on "hands-on" use of air sampling instruments. This course does not assume a background in air pollution.

For registration by July 8,1994 contact:

Thanh To
ORES Boulder
University of Colorado-Boulder
Campus Box 216
Boulder, CO 80309-0216
Tel: (303)-492-0357; Fax: (303)-492-1149

OR

Richard Graham
Morrison Knudsen Environmental
7100 E. Belleview Ave
Suite #300
Englewood, CO 80111
Tel: (303)-793-5068; Fax: (303)-290-0238

VENDOR WORKSHOPS

Bruker Instruments, Inc.

Second Annual Rocky Mountain Conference Workshop on Solid State NMR

Bruker Instruments will host a one day workshop dedicated to solid state NMR on Sunday, July 31 at the Hyatt Regency Denver hotel. New developments and products from Bruker will be presented, along with experimental results presented by users of Bruker instrumentation. All NMR spectroscopists with an interest in solids are encouraged to attend, regardless of whether they are familiar with Bruker Instruments or not. This should be an excellent opportunity to find out more about the current capabilities and future directions of Bruker in solids, and also for you to share your ideas on what you would like to see us offer in the future.

If you plan to attend, or would like more information, please contact Doug Burum at (508) 667-9580 x120.

Thermo Jarrell Ash Corporation

ThermoSPEC User's Seminar

Thermo Jarrell Ash will be holding it's annual user's seminar on Thursday, August 4. The format will be two-half day seminars for interested AA and ICAP users. Both seminars will provide new and exciting updates on software and applications as well as a question and answer session. The seminar is free and will include lunch.

To make reservations, please contact Loretta Beauvais at (303) 972-9814 by July 15.

Waters Chromatography

Practical Environmental Applications

Waters Chromatography offers a bench-level course on environmental applications of chromatography on Thursday, August 4. Topics include applications such as GPC Cleanup, Carbamate and Urea Pesticides, PAH's, Aldehydes and Ketones in both air and water, explosives, Nerve Agent Degradation Products, non-volatiles by HPLC/MS (both beam and thermospray), and Anionic Sulfonic Acids. The seminar is free!

Please call Denise Kent at (800) 645-5476 x6987 to register.

VENDOR WORKSHOPS

Buck Scientific / Western Analytical Instruments, Inc.

New Advances in High Performance Microwave Technology for Evaluation of Environmental and Production Materials

The advent of Microwave technology into the laboratory has given the chemist a way to bring the preparation up to the level of the analysis.

The MILESTONE series of products is specifically designed for the high throughput, difficult sample, maximum safety lab environment. The heart of the system is the 1200-MEGA Digestion Unit, which can accommodate several style of MDR digestion vessels, with pressure capacities from 425 to 1560 psi; for performing complete digestion or controlled leaching at fixed temperatures (per USEPA 3000 series protocols). Extractions, moisture and volatiles measurements can be made using the LAVIS-1000 system; using the unique MCR evaporation rotor and vacuum system. Rapid and precise dry ashings can be done in the 1200-PYRO unit in under 20 minutes at temperatures up to 1000°C.

With a focus on environmental materials, this seminar will also examine the use of microwave systems in the Manufacturing sector, as a product QC tool, and in Food Technology for both QC and research.

This seminar will be held on Sunday, July 31. The cost is $35.00, lunch is included. Please reserve your space by contacting Jim Viets at (303) 278-8346 or Bob Dhyse at (303) 794-0509 of Western Analytical Instrumentation, Inc.

Dionex Corp.

HPLC Applications and Validation Workshop

Discover exciting new HPLC techniques and instrumentation for environmental, pharmaceutical and research applications. Learn about new Data Workstation that will help you meet GMP, GLP / GALP, ISO 9000 and other regulatory requirements. It is powerful and easy to use!

This workshop will be held on Wednesday, August 3. To register or for more information, contact Lee Ramirez at (303) 771-2129. There is no charge for this workshop!

VENDOR WORKSHOPS

CEM Corp.

Microwave Technology Seminar

CEM will present an afternoon seminar on Wednesday, August 3,1994 exploring the use of microwave technology in the laboratory. The agenda for this seminar will be:

1. **Microwave Assisted Chemistry.**
2. **Advances in Microwave Sample Preparation Instrumentation.**
3. **Applications, Problems, Challenges and Solutions.**
4. **The Revolutionary New Idea: Automated Continuous Flow Microwave Digestion.**
5. **The Newest Frontier: Microwave Assisted Solvent Extraction.**

To make reservations for this seminar, or for further information, please contact Jay Leazer at (800) 726-3331.

Varian Associates

Varian NMR Instruments 3rd Conference for Solids System Owners and Users

Varian Solids Systems' Owners and Users are invited to a half day conference with Varian Application Scientists, R&D Engineers, and Product Managers on Sunday afternoon, July 31, 1994. There will be lectures on emerging applications and specific topics contributed by users. This is an excellent opportunity for long-term Varian customers and newcomers to gather for an afternoon of stimulating scientific interaction which will then adjourn for an evening of dining as guests of Varian. For registration materials, please call Ms. Bee Wallace in Palo Alto, CA at 415-424-4526. Please indicate if you wish to make a presentation. For other information regarding this conference, please contact the local account manager, Iain Green at (708) 945-3757.

VENDOR WORKSHOPS

Otsuka Electronics / Chemagnetics
5th Annual Solid State NMR Spectroscopy Workshop

Dates: **Friday, August 5 and Saturday, August 6.**

Location: **Otsuka Electronics / Chemagnetics**
2555 Midpoint Drive
Ft. Collins, CO 80525

Friday, August 5 **Solid State NMR Techniques and Applications**

Emphasis will be laid upon the practical aspects of various Solid State NMR techniques available to-date and the developments needed to enhance the reliability and applicability of NMR spectroscopy and imaging in solid material research. The workshop takes the form of a series of informal talks with ample time given for discussion.

Saturday, August 6 **Hands-on "New Techniques" Workshop**

DOR, Spinsight Software, Triple Resonance and other new tools will be discussed and demonstrated on CMX spectrometers. Small groups of attendees will work with several experiments and are encouraged to bring several of their own samples to run.

For further information contact: Dr. Jim Frye (303) 484-0428 (phone)
(303) 484-0487 (FAX)
jimf@otsuka.com (E-mail)

To register: **Complete the form below and return it to the address shown prior to June 30. There is no fee for this workshop, however local accommodations and mealr are at attendees expense.**

Please register me for this summer's Advanced Solid State NMR Workshop:

Name:

Phone

FAX:

Address:

Mail to: Pat Jones, Chemagnetics Products Group, 2555 Midpoint Dr., Ft Collins, CO 80525

SYMPOSIUM ON ATOMIC SPECTROSCOPY AND ICP-MS

Organized by Gary D. Rayson and Howard E. Taylor

Monday, August 1, 1994

Keynote Speaker

8:30 ***New Sources and Detection Systems for Atomic Mass Spectrometry,*** **Gary M. Hieftie. Indiana University, Bloomington, IN. (1)**

9:10 ***A new Technology in High Performance ICP-MS,*** **C. B. Douthitt. Finnigan MAT, Dallas, TX. (2)**

9:30 ***The Power of Elemental "Fingerprinting" Using the IRIS, a CDD Based ICP-AES,*** **J. E. Schmelzel and M. Pilon, Thermo Jarrell Ash Corp-, Franklin, MA. (3)**

9:50 BREAK

10:20 ***Relating Elemental and Algal Constituents ofEstuarine Waters Through Multivariate Analysis oflCP Mass Spectra,*** **M. E. Ketterer, J. R. Johansen and G. V. Sgro, Departments of Chemistry and Biology, John Carroll University, University Heights, OH. (4)**

10:40 ***Determination of Selenium in Blood Samples by GF-AAS,*** **Li Zhi-Min and Meng Lan-Xiang, Institute of Atomic Energy and China Imp./Exp. Commodity Inspection Technology Institute, Beijing, China. (5)**

11:00 ***High Resolution ICP-MS for Ultra Trace Analysis in Difficult Matrices,*** **C. B. Douthitt. Finnigan MAT, Dallas, TX. (6)**

11:20 ***Determination of Silicon Concentrations in WF(j Residue Samples by the Graphite Furnace Atomic Absorption Technique,*** **G. W. Johnson. Bandgap Chemical Corporation, Longmont, CO. (7)**

11:40 ***Determination of Selenium in Natural Water by GF-AAS after Solvent Extraction Pre concentration,*** **Li Zhi-Min and Meng Lan-Xiang, Institute of Atomic Energy and China Imp./Exp. Commodity Inspection Technology Institute, Beijing, China. (8)**

12:00 LUNCH

1:30 ***An Investigation into the Detection of Trace Metals in Refractory Sample Matrices Utilizing Inductively Coupled Plasma Co-axial Viewing Atomic Absorption Spectroscopy,*** **G. D. Rayson and C. E. Hensman, Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM. (9)**

1:50 ***Laser Vaporization with Resonant Excitation in Ultra-Trace Elemental Analysis—Application Towards Single Cells,*** **C. J. Smith and E. S. Yeung, Department of Chemistry and Ames Laboratory-USDOE, Iowa State University, Ames, IA. (10)**

2:10 ***Development of an Alternative Method of Measuring Excitation Temperatures Independent of Boltzman Equilibrium Assumptions: Applications and Implications,*** **G. D. Rayson and M. W. Duarte, Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM. (11)**

2:30 ***Vaporization and Atomization Mechanisms in the Graphite Furnace,*** **V. Nwogn. School of Physical Sciences, Abia State University, Uturu, Abia State, Nigeria. (12)**

2:50 ***Using An Advanced High Pressure Digestion Vessel as a New Approach to Microwave Sample Preparation of Reactive Sample Types,*** **Bob Fidler. Sara Littau, CEM Corp., P.O. Box 200, Matthews, NC. (403)**

SYMPOSIUM ON CHROMATOGRAPHY

Organized by Denise Kent

Wednesday, August 3, 1994

8:30 **Opening remarks.**

8:35 ***Optimization of Photodiode Array Detection and HPLC Mobile Phases For Detection Of Coeluting Impurities,*** **Jeanne B. Li and Richard L. Cotter, Water Chromatography, 34 Maple Street, Milford, MA, 01757. (13)**

9:05 ***New HPLC Method For The Determination OfPeroxyaceticAcid,*** **Ulrich Pinkernett, Uwe Karst. and Karl Cammann, Institute for Chemical and Biochemical Sensor Research, Westfalische Wilhelms-Universitat, Wilhelm-Klemm-Str. 8, 48149 Munster, Germany.Mailing address: CIRES, University of Colorado, Campus Box 216, Boulder, CO, 80309. (14)**

9:25 ***Analysis Of Nerve Agent Degradation Products Using Capillary Ion Electrophoresis,*** **Stuart Oehrle. Waters Chromatography, 34 Maple Street, Milford, MA, 01757. (15)**

9:45 ***Development of a Semi-Automated Clean-Up Procedure for the Determination of Polycyclic Aromatic Hydrocarbons (PAH's) in Ambient Air Samples,*** **Nick P. Alexandrou. and Kenneth A. Brice, Environment Canada, Atmospheric Service, 4905 Dufferin Street, Downsview, Ontario, M3H 5T4, Canada. (17)**

10:05 ***Extraction Efficiencies of Spiked versus Native PAHs From Wet Clay Using Standard Methods and A Closed Extraction Method,*** **Marshall P. Tilbury. Paul C. Winkler, and Donald C. Zapien, ENSECO/RMAL, 4955 Yarrow Street, Arvada, CO 80002. (404)**

10:25 ***Extraction Efficiencies and Aqueous/Solid Partition Ratios of PCBs in Sediment Waters via SPE andLLE,*** **Marshall D. Tilbury. Paul C. Winkler, and Donald C. Zapien, ENSECO/RMAL, 4955 Yarrow Street, Arvada, CO 80002. (405)**

SYMPOSIUM ON THE BIOGEOCHEMISTRY OF COMPOST

Organized by R. L. Wershaw and Cal Kuska

Monday, August 1, 1994

Cal Kuska, Presiding

8:20 Opening remarks

8:30 ***Mechanisms Regulating Composting of High Carbon to Nitrogen Ratio Grass Straw,*** **William R. Horwath and Lloyd F. Elliott, Oregon State University and USDA-ARS, Corvallis, Oregon 97331-7102 (18)**

9:00 ***Inoculation of Purely Cultured Thermophilic Bacterium, Bacillus licheniformis NAl, Aimed to Accelerate The Organic Matter Decomposition at The Early Stage of High Rate Composting,*** **Kiyohiko Nakasaki. Nobuyuki Uehara, Minoru Kataoka, and Hiroshi Kubota, Shizuoka University, Hamamatsu, Japan, and Tokyo Institute of Technology, Tokyo, Japan. (19)**

9:30 ***Relation Between Microbial Growth, Biomass Degredation and Trace Nutrient Availability During Composting,*** **Cheryl F. Atkinson. Kim L. Cook, Daniel D. Jones, Joseph J. Gauthier, Biology Dept., UAB, and Kenneth L. Blackwood, PWT Waste Solutions, Inc., Birmingham, AL 35294. (20)**

10:00 BREAK

10:30 ***The Quality of Source Separated Biogenic Waste Compost and The Effect on Soil and Plant Quality,*** **H. Vogtmann. K. Fricke, and A. Meier-Ploeger, University of Kassel, Witzenhausen, and University of Fulda, Germany. (21)**

11:00 ***Changes in Bacterial Populations During The Composting of Poultry Litter, Sawdust, Yard Waste, and Cotton Gin Trash,*** **Larry Softlev. Jr.. Willie McDaniel, Debra Tuten, Sheri Grosso, Cindy Kirsch, Richard Strickland, and Donald Roush, Tennessee Valley Authority, Muscle Shoals, Alabama, and University of North Alabama 35660, Florence, Alabama 35631 (22)**

11:30 ***Modification of Physical and Biological Properties of Soil by Addition of Household Waste Compost,*** **Claire Serra-Wittling. Sabina Houot, and Enrique Barriuso, Laboratoire des Sols, I.N.R.A., Thiverval-Grignon and Procter & Gamble France, Neuilly sur Seine Cedex, France. (23)**

12:00 LUNCH

Pierre Benoit, Presiding

1:30 ***Effects of the Use of Recycled Compost as Bulking Agent on the Microbial Flora of a Composting Process,*** **Kim L.Cook, Cheryl F. Atkinson, Daniel D. Jones, Kenneth Blackwood, Joseph J. Gauthier. Biology Department, UAB, Birmingham, AL 35294, and PWT Waste Solutions, Inc., 500 Southland Dr. Ste 124, Binningham, AL 35226-3711 (45)**

2:00 ***Feasibility of Bioremediating Pesticide/PCB/PAH-Contaminated Soils by Composting,*** **F. Kudio Dzantor. Tennessee Valley Authority, Muscle Shoals, Alabama 35660 (25)**

2:30 ***The Microbiology of Environmentally Controlled Composting of Separated Grease Trap and Food Related Sludge Waste Materials,*** **Russell S. Joshua. Barry J. Macaulay, and Craig R. Hudson, La Trobe University, Bundoora, Victoria, and C.R. Hudson & Associates Pty. Ltd., Surrey Hills, Victoria, Australia. (26)**

3:00 ***Remediation of Pesticide-Contaminated Soil with Compost,*** **Michael A. Cole. Xianzhang Liu, and Liu Zhang, University of Illinois, Urbana, Illinois 61801 (27)**

Tuesday, August 2, 1994

Michael A. Cole, Presiding

8:30 ***Enzymatic Incorporation of Pentachlorophenol into Humic Substances from Soil,*** **Carmen Ruttimann-Johnson and Richard T. Lamar, USDA-Forest Service, Forest Products Laboratory, Madison, Wisconsin 53705 (28)**

9:00 ***The Feasibility of Composting Wastes Contaminated with High Volatile PAH,*** **Ana E. Silveira and Rui B. Ganho, New University of Lisbon, Monte de Caparica, Portugal. (29)**

9:30 ***Environmentally Safe On-Farm Composting,*** **Christopher Lufkin and Ted Loudon. Michigan State University, East Lancing, Michigan 48824-1323. (30)**

10:00 BREAK

10:30 ***Effect of Straw Composting on The Degradation and Stabilization of Chlorophenok in Soil,*** **Pierre Benoit and Enrique Barriuso, Laboratoire des Sols, I.N.R.A., Thiverval-Grignon, France. (31)**

11:00 ***The Effects ofLignocellulose Structure and Composition on The Degradation and Mineralization ofAtrazine,*** **Nishant Rao and Hans E. Grethlein, Michigan State University, East Lansing, Michigan 48824 (32)**

11:30 ***Fate of Lawn Care Pesticides, 2,4-D andDiazinon During Yard Waste Composting,*** **Frederick C. Michel. Jr.. C. A. Reddy, and Larry J. Forney, Michigan State University, East Lansing, Michigan 48824 (33)**

12:00 LUNCH

Robert L. Wershaw, Presiding

1:30 ***Biodegradable Plastics in Composting,*** **Ludwig Streff and Werner Bidlingmaier Universitat Gesamthochschule Essen, Essen, Germany. (34)**

2:00 ***The Compostability of Biodegradable Plastics and Their Influence on Compost Quality,*** **H. Vogtmann and R. Gottschall, University of Kassel, Witzenhausen, Germany. (35)**

2:30 ***CPMAS 13C-NMR Spectroscopy as A Predictive Tool for Compost Stability and Soil Health,*** **Harry A. J. Hoitink. Larry V. Madden, and Ed G. Wilson, Ohio Agricultural Research and Development Center, Ohio State University, Wooster, Ohio 44691, and University of Akron, Akron, Ohio 44325 (36)**

3:00 BREAK

3:30 ***Mechanism of Adsorption on Alumina of A Compost Leachate DOC by Solid State 13C NMR,*** **Robert L. Wershaw. Elma C. Llaguno, and Jerry A. Leenheer, U.S. Geological Survey, Arvada, Colorado 80002-1800, USA and University of the Philippines, Diliman, Quezon City, Philippines. (37)**

4:00 ***Fluorescence Spectral and Lifetime Studies of Compost Leachates,*** **Sherry L.Hemmingsen and Linda B. McGown, Duke University, Durham, North Carolina 27708-0348 (38)**

4:30 ***Application of Spectroscopic Analysis to The Composting Process in A Bench Scale Composting System,*** **David Y. Tseng. Sam J. Traina, and Jeffrey J. Chalmers, Ohio State University, Columbus, Ohio 43210 (39)**

Wednesday, August 3, 1994

Robert L. Wershaw, Presiding

8:30 ***Analysis of Composts by Conventional and in situ Methylation Pyrolosis,*** **C. Saiz-Jimenez. A. Cegarra, B. Raig, B. Hermosin, J. J. Ortega-Calvo, C. Paredes, and M. P. Bernal, Instituto de Recusos Naturales y Agrobiologia, C.S.I.C., Sevilla and Centro de Edafologia y Biologia Aplicadadel Segura, C.S.I.C., Murcia, Spain. (40)**

9:00 ***Analysis of Inorganics and Semi-volatile Organics in Composted Waste Materials,*** **David E. Stilwell. Brian D. Eitzer, and Craig L. Musante, Connecticut Agricultural Experiment Station, New Haven, Connecticut 06504 (41)**

9:30 ***Bioavailability of Heavy Metals from Compost,*** **Philip R.Warman. Nova Scotia Agricultural College, Truro, Nova Scotia, Canada (42)**

10:00 BREAK

10:30 ***Identification and Quantification of Compost Market Space to "Unusage" Markets Based on Usage,*** **Rod Tyler. Kurtz Bros., Inc., Independence, Ohio 44125 (43)**

11:00 ***Influence of Management on Humification on Ferritic Soils ofNE Cuba,*** **Maria E. Rodriguez. Cuban Academy of Sciences, Havana, Cuba. (44)**

SYMPOSIUM ON ELECTROCHEMISTRY

Organized by Carl A. Koval

Tuesday, August 2, 1994

Session I - FUNDAMENTALS

8:30 ***Hot Electron Detection in Photoelextrochemical Cells with GaAs/AlGaAs Supperlatticel Electrolyte Junctions,*** **David K. Watts. Carl A Koval.(46)**

8:50 ***Measurement of Electrostatic Characteristics at Solid/Liquid Interfaces,*** **John M. Pope and Daniel A. Buttry. (47)**

9:10 ***Determination of Large Heterogeneous Rate Constants Using Nanoelectrode Ensembles,*** **Vinod P. Menon. Charles R. Martin. (48)**

9:30 ***Through-Space vs. Through-Bond Interactions in Rigidly Linked Homodinuclear Complexes,*** **Daniel Derr. Suzanne Ferrere, C. Michael Elliott. (49)**

9:50 ***Molecular Rectification of Current in Self-Assembled Redox Bilayers,*** **Jodv Redepenning. Jacqueline M. Flood, Efrain Castro-Narro. (50)**

10:10 BREAK

Session II - MATERIALS

10:30 ***Individual Microelectrode Behavior at Low Density Arrays of Microelectrodes,*** **C. Anthony Pitrat. Charles R. Martin. (51)**

10:50 ***Investigations into the La2Cu0$_{4}$^and Related Systems: Synthesis, Thin Film Preparation and Electrochemical Oxidation,*** **William J. Donahue. Bruce A. Parkinson, Robert L. Harlow, Michael K. Crawford, Eugene M. McCarron III. (52)**

11:10 ***Template Synthesis of Metal Nanoparticles and Optical Orientation Effects,*** **Deborah L. Kunkel. Vinod P. Menon, Charles R. Martin. (53)**

11:30 ***Optical Properties and Characterization of Aluminum Nanometal/Porous Aluminum Oxide Composite Thin Films: Transparency Throughout the Visible Region of the Spectrum,*** **Gabor L. Hornvak. K.L.N. Phani, Benjamin P. Berggren, Charles R. Martin. (55)**

11:50 LUNCH

Session m - SURFACE PROCESSES

1:30 ***Electrochemistry of Methanol at Low Index Crystal Planes of Platinum: An Integrated Voltammetric and Chronoamperometric Study,*** **Krzysztof Franaszcuk. Andrej Wieckowski. (56)**

1:50 ***Surface Electrochemistry of Dihydroxyquinones: Comparison of Pendent and Non-pendent 5,8-Dihydroxyquinone,*** **Donald C. Zapien. Trang Y. Vo, Angelique D. Willard. (57)**

2:10 ***Investigations of High Quality Quantum Yield Dye Sensitization Processes on a Two-Dimensional Semiconductor,*** **Laura J. Sharp. Xiumei Dou, Bruce A. Parkinson. (58)**

2:30 ***Surface Characterization of Immobilized Amines on Carbon Fiber Surface.*** **Jimmy CM. Peng. Daniel A. Buttry. (59)**

2:50 BREAK

Session IV - ANALYTICAL AND OTHER APPLICATIONS

3:10 ***Investigation of Changes in Redox Behavior of Conducting Polymers in the Presence of Neutral Organics,*** **Susan M. Hendrickson. Daniel L. Feldheim, Michael Krejcik, C. Michael Elliott. (60)**

3:30 ***Response Mechanism of Potentiometric Heparin Sensor: A New Approach for the Detection of Polyionic Macromolecules,*** **Bin Fu. MarkE. Meyerhoff. (61)**

3:50 ***Nickel Oxide Amperometry, Convection and Alkaline Earth Effects,*** **C.J. Gartzke, C.O. Huber. (62)**

4:10 ***A Study of a Series of Multicolor Electrochromic Ruthenium Complexes,*** **Frances Pichot. Jeff Beck. David Underwood, C. Michael Elliott. (63)**

4:30 ***A Useful Six-electron Reducing Agent? Synthesis and Characterizations of Metal Complexes with Alkylated Quaterpyridine Ligands,*** **Jody Redepenning, Sangsub Han. Marc A. Larson. (64)**

4:50 ***Separation and Concentration of Gases Utilizing Electrochemically Modulated Complexation,*** **Carl A. KovaL Patricia Terry, Richard D. Noble. (65)**

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

Organized by Maria Tikkanen

Sponsorship of this symposium by Finnigan MAT is gratefully acknowledged.

Tuesday, August 2, 1994

Maria Tikkanen, Presiding

8:30 **Opening Remarks**

8:35 ***A Comparison of Rural and Urban Aldehyde Concentrations,*** **Randolph Eisenhardt. CU-Denver, Chemistry Department, P.O. Box 173364, Denver, CO 80217-3364. (66)**

8:55 ***Supercritical Carbon Dioxide Extractions of Organic Contaminants from Low Level Mixed Waste at the Rocky Flats Plant, Colorado,*** **Paul Buckley. Robert Sievers, Barbara Watkins, Cooperative Institute for Research in Environmental Sciences (CIRES), Campus Box 216, University of Colorado, Boulder, CO 80309-0216. (67)**

9:15 ***A Comparison of Membrane and Cartridge Solid-Phase Extraction for Field Isolation of Trace Organic Compounds in Ground Water±*** **Janence C. Koleis. Edward Furlong, and Paul Gates, U.S. Geological Survey, 5293 Ward Road, Arvada, CO 80002. (68)**

9:35 ***A New Microwave Instrument for Rapid Solvent Extractions,*** **Todd Kierstead and Robert Revesz, CEM Corporation, P.O. Box 200, Mathews, NC 28106-0200. (69)**

9:55 ***Mass Spectral Confirmation of Drug Residues in Tissue of Farm-Raised Aquatic Species,*** **Sherri B. Turnipseed. Jose E. Roybal, Robert K. Munns, Heidi S. Rupp, David C Holland, Austin R. Long, Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Denver, CO 80225-0087. (406)**

10:15 **BREAK**

10:35 **Invited Speaker**
The Use of Liquid Chromatography/Mass Spectrometry for Environmental Analysis at the U.S. EPA, **Don Betowski. U.S. EPA, EMSL-Las Vegas, P.O. Box 93478, Las Vegas, NV 89193. (70)**

11:15 ***Ultra Trace Analysis in Complex Matrices by New Methods in Environmental Ion Trap Mass Spectrometry,*** **William C. Schnute, Finnigan Corporation, 355 River Oaks Parkway, San Jose, CA 95134. (72)**

11:35 LUNCH

Maria Tikkanen, Presiding

1:30 ***Field Comparisons of a Wet Effluent Denuder and Frit Method with a Filter Pack Method for the Measurement of Nitric Acid and Particulate Nitrate,*** **Susan M. Buhr. Fred C. Fehsenfeld, Richard B. Norton, and Robert Sievers, Aeronomy Laboratory, R/E/AL7, 325 S. Broadway, Boulder, CO 80303. (73)**

1:55 ***The Analysis of Marine Biotoxins in Shellfish,*** **Eoin P. Carmody, Kevin J. James and Sean S. Kelly, Chemistry Department, Cork Regional Technical College, Rossa Avenue, Bishopstown, Cork, Ireland. (74)**

2:15 ***The Determination of Mercury in Environmental Samples Using the Perkin-Elmer Flow Injection Mercury System,*** **S. Mcintosh, J. Baasner, C. Hanna, Perkin-Elmer Corp., 50 Danbury Road, Wilton, CT 06897-0219 and Randy Hergenreder. Perkin-Elmer Corp., 14818 W. 6th Avenue, Suite 6, Golden, CO 80401. (75)**

2:35 ***An Innovative Field Sampling Kit Developed for the Speciation of Aluminum in Natural and Treated/Distributed Water used for Human Consumption,*** **Jean-Charles Meranger. Denis G. Brule, and Belinda Lo, Health Canada, Environmental Centre, Tunney's Pasture, Ottawa, ON, K1A 0L2. (76)**

2:55 BREAK

3:15 ***Disinfection Kinetics in Drinking Water,*** **Charles N. Haas, Mark S.Heath, Joseph Jacangelo, Uma Anmangandla, Josh Joffe, Joel C. Homberger, Joseph dicker and Ruth L. Hund. American Water Works Association Research Foundation, 6666 W. Quincy Avenue, Denver, CO 80235. (77)**

3:35 ***"Almost Digestions" or Hot-Acid Leaches with Continuous Flow Microwave Sample Preparation,*** **Nancy Hoblack, Edward E. King, David Barclay, J. Douglas Ferguson, Lois Jassie, CEM Corporation, P.O. Box 200, Mathews, NC 28106-0200. (78)**

3:55 ***Analysis of Radionuclides in Environmental Samples by ICP-MS,*** **Rob Henry. Fisons Instruments, P.O. Box 20460, Boulder, CO 80308-3460. (79)**

Wednesday, August 3, 1994

Maria W. Tikkanen, Presiding

8:30 Opening Remarks

8:35 Invited Speaker

Regulatory and Health Issues with Upcoming Arsenic Drinking Water Standards, **Bruce Macler. USEPA Region IX, 75 Hawthorne Street, San Francisco, CA 94105. (80)**

9:15 ***Results of the Recent Low Level Arsenic Occurrence Survey in California,*** **M. W. Tikkanen. Association of California Water Agencies, 910 K Street, Suite 250, Sacramento, CA 98514 (81)**

9:35 ***Arsenic in Drinking Water: Occurrence, Speciation, Removal Options,*** **Michelle Fry, Black and Vetch and Marc Edwards, Department of Architectural, Civil and Environmental Engineering, University of Colorado, Boulder, CO 80309-0428. (82)**

9:55 ***Evaluation of the Practical Quantitation Level (PQL) for Arsenic using Atomic Absorption Spectrophotometry,*** **A. Eaton, Montgomery Laboratories, 555 E. Walnut, Pasadena, CA 91101 and M. W. Tikkanen. Association of California Water Agencies, 910 K Street, Suite 250, Sacramento, CA 95814. (83)**

10:15 BREAK

10:35 ***Analytical Chemistry of Arsenic in Drinking Water,*** **Jeff Oxenford. American Water Works Research Foundation, 6666 W. Quincy Avenue, Denver, CO 80235-3098, Andrew Eaton, Montgomery Laboratories, 555 East Walnut Street, Pasadena, CA 91101. (84)**

10:55 ***Selenium Mobilization by Irrigation in the Uncompahgre River Valley of West-Central Colorado,*** **K. C. Stewart. J. G. Crock, and R. C. Severson, US Geological Survey, Box 25046, MS 973, Federal Center, Denver, CO 80255. (85)**

11:15 ***Survey of Lead in Environmental Matrices by Atomic Spectroscopy Techniques,*** **Zoe A. Grosser, Perkin-Elmer Corp., 50 Danbury Rd., Wilton, CT 06897-0219 and Randy Hergenreder. Perkin-Elmer Corp., 14818 W. 6th Avenue, Suite 6, Golden, CO 80401. (86)**

11:35 ***Application of Geochemical Modeling to Proposed Methods of Dissolved Lead Removal From a Mine Drainage,*** **Beth McMillan, Ronald W. Klusman, and Thomas R. Wildeman, Colorado School of Mines, Golden, CO 80401. (87)**

17th INTERNATIONAL EPR SYMPOSIUM

Organized by Gareth R. Eaton and Sandra S. Eaton

Sunday, July 31, 1994

6:00 - 10:00 pm Open House at University of Denver EPR Laboratory.

We invite you to see our new ESP380 spectrometer, chat with fellow spectroscopists, and enjoy refreshments including German beer, courtesy of Bruker Instruments. Transportation will be provided from and to the Hyatt Hotel.

Monday, August 1, 1994

Session I - Keith McLauchlan, presiding

8:30 **Welcomes by Sandra Eaton and Kev Salikhov**

8:40 **Presentation of International EPR Society Gold Medal by Keith McLauchlan, President**

8:45 **Award address:** ***Recent Developments in and Applications of Two Dimensional and High-Field ESR,*** **by Jack H. Freed. Cornell University. (88)**

9:30 ***Probing Structure and Dynamics in Peptides with Site Specific ESR Spin Labeling,*** **by Glenn L. Millhauser. University of California, Santa Cruz. (89)**

10:10 **Break**

10:40 ***"2+1" SECSY - A New Variety of 2D Pulse Adjusting Spectroscopy,*** **by Arnold Raitsimring. Richard H. Crepeau, and Jack H. Freed, University of Arizona and Cornell University. (90)**

11:10 ***Analysis of One- and Two-Dimensional EPR Spectra in the Slow-Motion Regime Using the Model Trust-Region Least-Squares Algorithm,*** **by David E. Budil. Sanghyuk Lee, and Jack H. Freed, Northeastern University and Cornell University. (91)**

11:40 ***Low Temperature Dynamics of a Nitroxide Spin-Probe in Porous Materials,*** **by Claude Chachaty. Centre d'Etudes de Saclay. (92)**

12:00 **Lunch**

Session II - Karl Hausser, presiding

1:30 **Presentation of International EPR Society Silver Medal by Karl Hausser, Awards Committee**

1:35 **Award address:** ***Studies of Transient Free Radicals in Solution.- Limitations and Advantages of ESR Methods,*** **by Keith McLauchlan. Oxford University. (93)**

2:20 ***Inversion-Recovery of Nitroxide Radicals in Solution,*** **by Nicholas J. Turro, Igor V. Koptyug. and Stefan H. Bossmann, Columbia University, Institute of Chemical Kinetics and Combustion, Novosibirsk, and Engler-Bunte Institute, Karlsruhe. (94)**

2:40 ***Pulsed and CWEPR Study of the Molecular Motion of a Phenalenyl Spin Probe in Cation-Exchanged Faujasite Zeolites,*** **by David C. Doetschman, David W. Dwyer. and Steven G. Utterback, Bingham ton University, SUNY at Brockport, and Hostos Community College. (95)**

3:00 Break

3:30 ***Anomalous Temperature Dependence of Tetrahedral Cobalt(II) Electron Spin Resonance in Aluminophosphate-5 Molecular Sieves,*** **by Vadim Kurshev and Larry Kevan, University of Houston. (96)**

3:50 EPR Studies of Ion-Exchanged Zeolites, **by Sarah C. Larsen. Adam Aylor, Alexis T. Bell, and Jeffrey A. Reimer, University of California Berkeley.(97)**

4:10 ***Application of ESR to Study the Hydrogenation of Alkenes and Benzene over a Supported Pd Catalyst,*** **by Albert Carley, Hywel Edwards, Fred E. Hancock, S. David Jackson, Brynmor Mile, M. Wyn Roberts, and Christopher C. Rowlands, University of Wales and ICI Katalko.(98)**

4:30 Kev Salikhov, Zavoiski Institute

4:50 International EPR Society Business Meeting, Keith McLauchlan presiding

5:30 Mixer in Exhibit and Poster area

Session III - posters, S. S. Eaton, presiding

7:00 - 8:00 Authors Present For Posters Labeled A
8:00 - 9:00 Authors Present For Posters Labeled B

(Posters are listed alphabetically by presenting author)

A ***An Investigation of Stable Free Radicals in Polyimides Using 250 GHz ESR Spectroscopy,*** **by Myong K. Ahn. Mary Ann Meador, David E. Budil, Keith A. Earl, Joe Moscicki, and Jack H. Freed, Indiana State University, NASA Lewis Research Center, and Cornell University. (99)**

B ***EPR Evidence for Binding ofCupric Ion to MAX,*** **by William E. Antholine. Chakravarathy Narasimhan, Kent W. Wilcox, Hongbing Wang, and Timothy Herman, Medical College of Wisconsin. (100)**

A ***Reaction ofDioxygen with the Nitric Oxide Adduct of Ferrous Bleomycin Bound to DNA,*** **by M. Claire Kennedy, William E. Antholine. Qunkai Mao, and David H. Petering, Medical College of Wisconsin and University of Wisconsin-Milwaukee. (101)**

B ***Saturation Recovery EPR of a Mutant of Nitrous Oxide Reductase,*** **by S. Pfenninger, W. E. Antholine. C. C. Felix, J. S. Hyde, P. M. H. Kroneck, and W. G. Zumft, Medical College of Wisconsin, University of Konstanz, and University of Karlsruhe.(102)**

A ***EPR/Spin Label Technique as an Analytical Tool for Determining the Resistance of Reactive Topical Skin Protectants (rTSPs) to the Breakthrough of Vesicant Agents,*** **by Carmen M. Arroyo. US Army Medical Research. (103)**

B ***Activation of Alpha-Human Tumor Necrosis Factor (TNF-a) by Human Monocytes (THP-1) Exposed to 2-Chloroethyl Ethyl Sulfide (H-MG),*** **by Carmen M. Arroyo, and Robert L. Von Tersch, US Army Medical Research. (104)**

A ***EPR Study of Point Defect Production of Vitreous Silicon Dioxide,*** **by William R. Austin and Robert G. Leisure, Colorado State University. (105)**

B ***Electron Spin Echo Modulation Spectroscopic Evidence for Framework Substitution ofNi(l) in NiAPSO-11,*** **by Naoto Azuma. Chul Wee Lee, and Larry Kevan, University of Houston. (106)**

A ***An EPR Study of the Structure of Surface Bound Surfactant Aggregates Involved in Shear Flocculation,*** **by Martin G. Bakker. Dexter D. Murphy, Terry Clark, Brandon Davis, and D. R. Spears, University of Alabama and U.S. Bureau of Mines. (107)**

B ***Continuous Wave and Spin Echo EPR Spectroscopy ofMn^· in ras p21 with ^ Labeling at 5 T,*** **by Brendan F. Bellew. Christopher J. Halkides, Gary J. Gerfen, Robert G. Griffin, Alfred G. Redfield, and David J. Singel, MIT. (108)**

A ***Powder ENDOR Studies of Disubstituted 1,4-Napthosemiquinones,*** **by Chris Bender and Gerald T. Babcock, Albert Einstein College of Medicine and Michigan State University. (109)**

B ***Spectroscopic Studies of the Charge-Transfer Reactions of Strong Electron Acceptors and Lecithin,*** **by Chris Bender. Albert Einstein College of Medicine. (110)**

A ***New Pulse EPR Spectrometer at University of Arizona,*** **by P. Borbat and A. Raitsimring, University of Arizona. (Ill)**

B ***Magnetic Resonance Studies on the Water Exchange Rate of Gadolinium-Based Contrast Agents: Modulation of Chemical Exchange Due to Binding to Human Serum Albumin,*** **by T. E. Bowers. N. V. Tsekos, J. H. Hwang, R. B. Clarkson, and R. L. Belford, University of Illinois. (112)**

A ***Delocalization of Unpaired Electrons in Acceptor-Bridge-Donor Molecular Structures as Monitored by EPR Spectroscopy,*** **by R. Krzyminiewski, A. Bielewicz, J. Kudynska, and H. A. Buckmaster. Adam Mickiewicz University and University of Victoria. (113)**

B ***Exploratory 9 GHz CW-EPR Oxidation Studies of Selected Commercial Motor Oils,*** **by J. Kudynska and H. A. Buckmaster. University of Victoria. (114)**

A ***Low Temperature Oxidation Kinetics of an HV Bituminous Coal as Studied by Dynamic in situ 9 GHz CW-EPR Spectroscopy,*** **by J. Kudynska and H. A. Buckmaster. University of Victoria. (115)**

B ***EPR, ENDOR, and ESEEM Studies on the Rieske Iron-Sulfur Proteins of Benzene Dioxygenase,*** **by Jasvinder K. Shergill, Clive S. Butler, Stephen Seah, Andrew C. White, Jeremy R. Mason, and Richard Cammack. University of London. (116)**

A ***Reductive Nitrosylation of Oxo-Chromium(V) Bis(2-ethyl-2-hydroxybutyrate) by Hydroxylamine,*** **by Lenny M. Carruthers. Christina L. Closken, Surendra N. Mahapatro, Sandra S. Eaton, and Gareth R. Eaton, Regis University and University of Denver. (117)**

B ***Computer Assisted ESR Study of the Ordering and Dynamics ofDoxylstearic Probes in Asymmetric Phospholipid Bilayers,*** **by Claude Wolf and Claude Chachaty. Centre d'Etudes de Saclay. (118)**

A ***Construction of a Cylindrical "Ribbon-Wound" EPR Q-band Cavity,*** **by Wenge Wang and Nj. Dennis Chasteen. University of New Hampshire. (119)**

B ***A Single Crystal EPR and ESEEM Analysis of Cu(II)-Doped bis(L-Histidinato) Cadmium Dihydrate,*** **by Michael J. Colaneri and Jack Peisach, Albert Einstein College of Medicine. (120)**

y\ *Two Dimensional Fourier Transform ESR Applied to Lipid Dispersion Samples: Experimental Advances,* by Richard H. Crepeau. Sunil Saxena, Sanghyuk Lee, Baldev Patyal and Jack H. Freed, Cornell University. (121)

B *"In Situ " EPR Analysis of Hydrogenated Carbon Thin Films,* by Mark Hoinkis and Mark Crowder, IBM Research. (122)

A *Quantitation of Coal and Diesel Soot by High Frequency (W-band) EPR Spectroscopy,* by Naresh Dalai, Alex I. Smirnov. and R. Linn Belford, West Virginia University and University of Illinois. (123)

B *Resolution of Overlapping Spin Label Spectra by CW Saturation Provides Access to the Depth Profile ofLipid-Protein Interactions,* by Lauraine A. Dalton and Keith W. Miller, Harvard Medical School and Massachusetts General Hospital.(124)

A *ESEEM Spectroscopy of Remote Nitrogens in Cu^^-(Imidazole)4 and Superoxide Dismutase,* by Sergei A. Dikanov. Andrei P. Spoyalov, Isabella Felli, Maria-Silvia Viezzoli, and Jurgen Huttermann, Institute of Chemical Kinetics, Novosibirsk, University of Florence, and Saarland University. (125)

B *Orientation Dependence of Electron Spin Lattice Relaxation Rates for Nitroxyl Radicals and ChromiumfV) Porphyrins in Frozen Solution,* by Jing-Long Du. Rachel I. Konda, Sandra S. Eaton, and Gareth R. Eaton, University of Denver. (126)

A *250 GHz EPR Studies of Polarity Gradients Along the Aliphatic Chains in Phospholipid Membranes,* by Keith A. Earle. Josef K. Moscicki, Mingtao Ge, David E. Budil, and Jack H. Freed, Cornell University. (127)

B *EPR Study of the Electrochemical Reduction of a Diphosphaalkene Chelating Agent and of its Palladium and Platinum Complexes,* by Michel Geoffroy. Abdelaziz Jouaiti, Gustavo Terron, and Gerald Bernardinelli, University of Geneva. (128)

A *High-Frequency (139.5 GHz) EPR Investigation of Short Alanine-Based Peptides in Aqueous Solution,* by Gary J. Gerfen. Gary V. Martinez, Glenn L. Millhauser, Robert G. Griffin, and David J. Singel, MIT, University of California, Santa Cruz, and Harvard University. (129)

B *Electron Spin Relaxation of Irradiated Fused Quartz at Four Frequencies,* by Barnard Ghim. Susanne Pfenninger, Richard W. Quine, Gareth R. Eaton, and Sandra S. Eaton, University of Denver and Medical College of Wisconsin. (130)

A *Spin Trapping Hydroxyl Radicals Generated by Ionizing Radiation in the Tumor of a Living Mouse with Very Low Frequency EPR,* by H. J. Halpern. C. Yu, E. Barth, M. Peric, and G. M. Rosen, University of Chicago and University of Maryland. (131)

B *Anisotropic Spin Lattice Relaxation Times - [3Fe-4S]l+ Ferredoxin From Giardia Duodenalis,* by Stephen M. Townson, Graeme R. Hanson, Jacqueline A. Upcroft, Peter Upcroft, Y. C. Zhong, and John R. Pilbrow, Queensland Institute of Medical Research, University of Queensland, and Monash University. (132)

A *Multifrequency EPR Studies of Mononuclear and Binuclear Copper(II) Patellamide Complexes and the Importance of Magic Angles,* by Anna L. van den Brenk, Graeme R. Hanson. Lawrence R. Gahan, and Clifford J. Hawkins, University of Queensland. (133)

B *The Active Site of Hydroxylamine Oxidoreductase: Evidence from Integer-Spin EPR for a New Metal Cluster in Proteins,* by Michael P. Hendrich. Michael Logan, Dave M. Arciero, Kristoffer K. Andersson, John D. Lipscomb, and Alan B. Hooper, University of Minnesota. (134)

A *A High Frequency CW and Pulsed EPR Spectrometer Based on an X-Band Intermediate Frequency,* by P. Hofer. K. Kolczer, M. Kloza, and D. Schmalbein, Bruker Instruments and University of California, Low Angeles. (135)

B *Electron and Nuclear Spin Relaxation Effects in Pulsed ENDOR Spectroscopy,* by P. Hofer. Bruker Instruments. (136)

A *Solvent Effects on the g Anisotropy of Semiquinone Radicals: EPR at Very High Frequency,* by A. Jain. M. J. Nilges, and R. L. Belford, University of Illinois. (137)

B *Chemical and Heisenberg Exchange in Ion Pair Solutions Revisited by Two Dimensional EPR Spectroscopy,* by S. Kababva. Z. Luz, and D. Goldfarb, Weizmann Institute of Science. (138)

A *Electron Spin Resonance Studies of the Photooxidation of Phenothiazine Derivatives in Silicas of Different Pore Sizes,* by Bosong Xiang and Larry Kevan. University of Houston. (139)

B *An ENDOR Study of Synthetic Carotenoid Cation Radicals,* by A. S. Jeevarajan, L. Piekara-Sady, M. Plato, and Lowell D. Kispert. University of Alabama and Freie Universitat Berlin. (140)

A *EPR Study ofFe Doped and H⁻ Implanted Indium Phosphide,* by W. Kevin Kuhn and Margaret H. Rakowsky, Frank J. Seiler Research Laboratory. (141)

B *Four-Puke Electron Spin Echo Envelope Modulation Studies of Ni(III)(CN)4^20)2",*by Hong-In Lee and John McCracken, Michigan State University. (142)

A *EPR Study of Three E' Variants in Microelectronic Quality Thin Film Thermal S1O2 on Si, by* John F. Conley, Jr., Patrick M. Lenahan. Howard L. Evans, Robert K. Lowry, and Thomas J. Morthorst, Pennsylvania State University and Harris Semiconductor. (143)

B *ENDOR and ESEEM Studies ofMn(II)ADP Complexes in Myosin,* by Jeanne Digel, Russell LoBrutto. Ivan Rayment, Robert Smith, L. Timothy Laughlin, and George H. Reed, Northeastern University, Arizona State University, and University of Wisconsin at Madison. (144)

A *Spin Coupling in Dinitroxyl Derivatives ofDiaza-Crown Ethers: Effect of Bivalent Ions Binding,* by Irina I. Lobysheva. Anatoly B. Shapiro, and Michael G. Goldfeld, Institute of Chemical Physics, Moscow. (145)

B *Temperature Dependent Pulsed EPR Relaxation Studies of the S2 State Multiline Signal of the Photosynthetic Oxygen Evolving Complex,* by Gary A. Lorigan and R. David Britt, University of California at Davis. (146)

A *Local Rearraangement of a Crystal Lattice Near Impurity Ions and Its Influence on Magnetic Properties of Crystals,* L.K. Aminov. Kazan State University, Kazan, Tatarstan-Russia 420008. (407)

B ***An Industrial Application of EPR: Nearly Continuous Study of Propagating Radicals in Batch Emulsion Polymerization ofMMA,*** **Hsiu-Rong Chang. Davie G. Westmoreland, Rohm and Haas Company, 727 Norristown Road, Spring House, PA 19477-0904, Hsing-Yeh Parker, Rohm and Haas Company, Rt. 13 and 413, Bristol, PA, 19007. (408)**

A ***Anomalies in Fluorine and Nitrogen Hyperfine Splitting Constants ofNitroxides in Various Solvents,*** **Jane Z. Chen. Yong-Kang Zhang, Uwe M. Oehler, Edward G. Janzen, Oklahoma Medical Research Foundation, National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, 825 NE 13th St., Oklahoma City, OK 73104, USA. University of Guelph, MRI Facility, Ontario Veterinary College, Guelph, Ontario, Canada NIG 2W1. (409)**

B ***Multifrequency Endor of a Nitroxide,*** **T. Christidis, Physics Department, American University of Beirut, 850 Third Ave., New York, NY 10022, James S. Hyde, Biophysics Institute, Medical College of Wisconsin, Milwaukee, WI 53226. (410)**

A ***A Multifrequency Endor Study of Fluoride Binding of Hemoproteins,*** **Yang C. Fann. Judith M. Nocek, Jui-lin Ong, and Brian M. Hoffman, Department of Chemistry, Northwestern University, Evanston, IL 60208-3113. (411)**

B ***Characterization of Iron (II) Dithiocarbamates as Nitric Oxide Spin Traps,*** **Yashige Kotake. Tom Tanigawa, Mari Tanigawa, Ucuko Ueno and Edward G. Janzen, National Diomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, Oklahoma Medical research Foundation, Oklahoma City, Oklahoma 73104. (412)**

Tuesday, August 2, 1994
Session IV - Harold M. Swartz, presiding

8:30 ***Electron Spin Resonance Investigations of Free Radical Toxicology,*** **by Ronald P. Mason. National Institute of Environmental Health Sciences. (147)**

9:00 ***Twenty-Five Years of Spin Trapping,*** **by Edward G. Janzen. Oklahoma Medical Research Foundation and University of Guelph. (148)**

9:30 ***Multi-Faceted ENDOR Spectroscopy ofMetalloenzymes,*** **by Clark E. Davoust, Victoria J. DeRose, Peter E. Doan, Yang-Cheng Fann, Jennifer Huyett, Bradley E. Sturgeon, Joshua Telser, and Brian M. Hoffman. Northwestern University. (149)**

10:00 Break

10:30 ***Structure and Dynamics in Membrane Proteins,*** **by Christian Altenbach and Wayne Hubbell, University of California, Los Angeles. (150)**

11:00 ***In Vivo Imaging with Very Low Frequency EPR: Progress and Implications for Future Measurements,*** **by H. J. Halpern. C. Yu, E. D. Barth, M. Peric, W. E. Boisvert, S. Kasa, M. W. Makinen, S. Pou, G. M. Rosen, University of Chicago and University of Maryland. (151)**

11:30 ***Melanin and Neuromelanin - A Biophysical Perspective,*** **by Tadeusz Sarna. Jagiellonian University. (152)**

12:00 Lunch

Session V- James S. Hyde, presiding

1:30 Presentation of International EPR Society Silver Medal by Keith McLauchlan, President

1:35 Award Address: *In Vivo EPR Spectroscopy: Progress and Potential Further Developments,* by Harold M. Swartz. Dartmouth Medical School. (153)

2:20 *Oximetry Studies Using 3D/4D Spectral-Spatial EPR Imaging of Biological Organs and Tissues at L-Band,* by Periannan Kuppusamv. M. Chzhan, and Jay L. Zweier, Johns Hopkins Medical Institutions. (154)

2:40 *Selective Hole Burning and its Application to Photosynthesis,* by Asako Kawamori. Yoshio Kodera, and Sergei A. Dzuba, Kwansei Gakuin University and Institute of Chemical Combustion, Novosibirsk.(155)

3:00 Break

3:30 *EPR and ENDOR Studies of the Electronic Structure of Pigment Radical Ions in Native and Genetically Modified Bacterial Reaction Centers,* by F. Lendzian, J. Rautter, H. KaB, F. Muh, M. Kuhn, J. P. Allen, and W. Lubitz, Technical University of Berlin and Arizona State University. (156)

3:50 *2JJ Electron Spin Echo Envelope Modulation Studies of Strong a-Hydrogen Hyperfine Coupling in Organic Radicals,* by Kurt Warncke and John McCracken. Michigan State University. (157)

4:10 *The Mechanism of Hydrolysis of P-Lactam Antibiotics: Structures of a Spin-Labeled Penicillin and its Hydrolytic Reaction Intermediates Determined by ENDOR,* by Devkumar Mustafi and Marvin W. Makinen, University of Chicago. (158)

4:30 *EPR Metrology at NIST,* by Marc F. Desrosiers. Debra L. Bensen, and James M. Puhl, National Institute of Standards and Technology. (159)

4:50 Yuri Tsvetkov

5:10 Software Issues Roundtable - Richard Cammack and Philip D. Morse, presiding

Tuesday evening - Dinner to recognize recipients of International EPR Society Gold and Silver Medals: Jack H. Freed, Wojciech Froncisz, Keith McLauchlan, and Harold Swartz.
All attendees are invited, contact G.R. or S.S. Eaton for details.

Wednesday, August 3, 1994
Session VI, joint with NMR Symposium, Hans Thomann, presiding

8:30 *High Frequency Dynamic Nuclear Polarization and Electron Paramagnetic Resonance,* by L. R. Becerra, G. Gerfen, J. Bryant, B. F. Bellew, D. Hall, S. Inati, K. J. Kreischer, R. J. Temkin, D. J. Singel, and R. G. Griffin. MIT and Harvard University. (160)

9:00 *Pulsed ENDOR Spectroscopy of ^{57}Fe Containing Zeolites,* by D. Goldfarb. M. Bernardo, K. G. Strohmaier, and D. E. W. Vaughan, Weizmann Institute and Exxon Research. (161)

9:30 *Dynamic Nuclear Polarization by Solvent Nuclei in Solutions Containing Free Radicals,* by *JjL* D. Bates. Jr.. Georgetown University. (162)

10:00 Break

10:30 ***Selective Observation of Silica Surfaces by ^Si Dynamic Nuclear Polarization/Magic Angle Spinning NMR,*** **by J. Kobayashi, Mitsubishi Electric Corp.(163)**

11:00 ***Advances and New Applications in High Frequency Puked EPR and Puked ENDOR Spectroscopy,*** **by J. Schmidt. University of Leiden. (164)**

11:30 ***Solid State NMR and Puked Electron Nuclear Multiple Quantum Spectroscopic Studies of Fullerene Polymer Interfaces,*** **by A. Afeworki, M. Bernardo, and H. Thomann. Exxon Research. (165)**

12:00 Lunch

Session VII, Bruce McGarvey, presiding

1:30 ***The Use of ENDOR to Identify the Atomic Structure of Defects in Diamond,*** **by J. M. Baker and M. E. Newton, Oxford University. (166)**

1:50 ***Very-High Frequency EPR: Calculation of g- and A-Tensors; from Httckel Theory to Ab Initio,*** **by M. J. Nilges. R. L. Belford, W. Wang, and R. B. Clarkson, University of Illinois. (167)**

2:10 ***High Spin Iron at High Frequency: Multiple Transitions and Predicted Effects of Parameter Distributions at 9-250 GHz,*** **by K. S. Doctor, B. J. Gaffnev. and J. H. Silverstone, Johns Hopkins University. (168)**

2:30 Break

Session VIII, posters, Wolfgang Trommer, presiding.
3:00 - 4:00 Authors Present For Posters Labeled C
4:00 - 5:00 Authors Present For Posters Labeled D

C ***Multifrequency Puked EPR Studies of the Primary Donor in Photosystem I Reveal a Histidine Ligand,*** **by Michelle Mac. Xiao-song Tang, Bruce A. Diner, Gerald T. Babcock, and John McCracken, Michigan State University and Dupont Central Research. (169)**

D ***Time-Resolved Electron Spin Resonance Studies of Spin Trapping: The Reaction ofAlkyl Radicak with DMPO,*** **by Keith P. Madden and Hitoshi Taniguchi, University of Notre Dame.(170)**

C ***EPR Single Crystal Study of the Fe(III)-0-Fe(III) Dimer in Two Systems,*** **by Andrzej Ozarowski, and Bruce R. McGarvey. University of Windsor. (171)**

D ***Angular and Temperature Dependences of Spin-Lattice Relaxation in 2D Molecular Composites,*** **by A. Niang, Guy Ablart, Jacques Pescia, Sushi! K. Misra. R. Duplessix, and N. B. Chanh, Universite Paul Sabatier, Concordia University, and University de Bordeaux. (172)**

C ***Variable Temperature EPR Study of NiiCdCl^. 12H,0 Single Crystal,*** **by Sushil K. Misra. Lucjan E. Misiak, and Prem Chand, Concordia University and Indian Institute of Technology. (173)**

D *Conformation ofDoxyl Stearic Acid Nitroxides in Vacuum, Water, and Hexane,* by Jean M. Standard, Janeice S. Ives, and Philip D. Morse II. Illinois State University. (174)

C *Improved Sample Handling for Cell Studies Using High-Frequency EPR,* by Philip D. Morse II and Alex I. Smirnov, Illinois State University and University of Illinois. (175)

D *Characterization of Mineral Surfaces by EPR,* by Dexter D. Murphy. Martin G. Bakker, Terry Clark, Brandon Davis, and D. R. Spears, University of Alabama and U.S. Bureau of Mines. (176)

C *Characterization of Calcium Binding Sites in Kidney Stone Inhibitor Glycoprotein (Nephrocalcin) with Vanadyl Ion by EPR and ENDOR Spectroscopy,* by Devkumar Mustafi and Yasushi Nakagawa, University of Chicago. (177)

D *An Evaluation of New Carbonaceous Oxygen-Sensitive EPR Probes* by Shong-Wan Norby. Anthony A. Lizzio, and Robert B. Clarkson, University of Illinois. (178)

C *EPR Investigation on Photo-Irradiation and Anisotropic Hyperfine Interaction of Vanadium Bronzes,* by Keiichi Ohno, Yasuyuki Morita, and Yoshikazu Kaneko, The Polytechnic University, Sagamihara and Yamanashi University. (179)

D *EPR and EPR Imaging of Phthalocyanine-Li Single Crystal Using Microcoil,* by Keiichi Ohno. Yasuyuki Morita, Masaaki Aoyama, and Masao Kohno, The Polytechnic University, Sagamihara, Yamagata Technopolis, and JEOL Ltd. (180)

C *Nitroxide Spin Probe/Label Study of Hydrogen Bonding and Probe Size Effects in a Linear Polymer,* by M. D. Pace and A. W. Snow, Naval Research Laboratory.(181)

D *Programmable Timing Unit,* by Richard W. Quine. University of Denver. (182)

C *Multiple Frequency EPR Studies of Novel Compounds with Two Weakly Coupled Spin=1/2 Metal Centers,* by Arnold M. Raitsimring. Partha Basu, and John H. Enemark, University of Arizona. (183)

D *Preliminary Results of the Study ofTb^+ Phase Relaxation in Silicate Glasses,* by Igor A. Gromov, Sergei B. Orlinskii, Rafail M. Rakhmatullin. and Urii M. Rosentzvaig, Kazan State University. (184)

C *Electron Spin Echo Decay: A Probe of Electron-Electron Spin-Spin Interaction in Spin-Labeled Iron Porphyrins,* by Margaret H. Rakowsky. Gareth R. Eaton, and Sandra S. Eaton, University of Denver. (185)

D *^{55}Mn ESE-ENDOR of Orientationally Disordered Manganese Complexes,* by David W. Randall. Bradley E. Sturgeon, James A. Ball, and R. David Britt, University of California, Davis. (186)

C *A Systematic Approach for Studying Cu Imidazole Interactions Using Multi-Frequency ESEEM; Applications to Cu-Bleomycin,* by Pieter J. van Dam, Edward J. Reiierse. and Engbert de Boer, University of Nijmegen. (187)

D *New Insight into the Structure ofNitrosyl Hemoglobin and its Model Compounds as Studied by ESEEM,* by Sergei A. Dikanov, Alexei M. Tyryshkin, Edward J. Reiierse. Christian Burgard, and Jurgen Huttermann, Institute of Chemical Kinetics and Combustion, Novosibirsk, University of Nijmegen, and Universitat de Saarlandes. (188)

C ***L-Band Loop Gap Resonator Design for Low-Temperature Experiments,*** **by George A. Rinard. Barnard Ghim, and Gareth R. Eaton, University of Denver. (189)**

D ***Magnetic Properties of Triplet Copper(II) and Oxovanadium(IV) Porphyrin Cation Radical Complexes,*** **by Minora Satoh. Keiko Ise, Fujio Ebina, Yasunori Ohba, Seigo Yamauchi, Mikio Hoshino, and Masamoto Iwaizumi, Ibaraki College of Technology and Tohoku University. (190)**

C ***The Three-Term Model for Ferric Iron and g-Strain EPR Simulations: Distributions of Crystal Field Parameters,*** **by Charles E. Schulz and Peter G. Debrunner, Knox College and University ofIUinois.(191)**

D ***The Coordination of Copper Ions to Hydroxamate Binders,*** **by V. Koffman, J. J. Shane. S. A. Dikanov, A. Haran, J. Libman, A. Shanzer, and D. Goldfarb, Weizmann Institute of Science and Institute of Chemical Combustion and Kinetics, Novosibirsk. (192)**

C ***Design of a Versatile Pulsed ENDOR Spectrometer,*** **by J. J. Shane. D. Goldfarb, and S. Vega, Weizmann Institute of Science. (193)**

D ***Thermal Phase Transitions in DPPC Liposomes as Studied by High-Frequency EPR,*** **by Alex I. Smirnov. Tatyana I. Smirnova, and Philip D. Morse II, Illinois State University and University of Illinois. (194)**

C ***Rapid Quantitation of Inhomogeneously Broadened EPR Spectra by a Fast Convolution Algorithm,*** **Alex I. Smirnov and R. Linn Belford, University of Illinois. (195)**

D ***EPR Imaging of Natural Free Radicals in Roasted Coffee Bean,*** **by Alex I. Smirnov and Philip D. Morse II, University of Illinois and Illinois State University. (196)**

C ***W-Band (95-GHz) EPR ofNitroxides with Complex Superhypetfine Structure: Fast Motion,*** **by Tatvana I. Smirnova. Alex I. Smirnov, and R. Linn Belford, University of Illinois. (197)**

D ***EPR of Some Vedrazyl Free Radicals: Low Dimensional Behavior,*** **by Alan Katritzky, Tatvana I. Smirnova. Sergei Belyakov, R. Linn Belford, and Naresh Dalai, University of Florida, University of Illinois, and West Virginia University. (198)**

C ***Half-Field EPR Transitions in Synthetic Carbohydrate Chars,*** **by Tatvana I. Smirnova. Alex I. Smirnov, R. B. Clarkson, and R. Linn Belford, University of Illinois. (199)**

D ***Near Optimal Projection Angle Selection by Minimum Entropy Criterion in EPR Image Reconstruction,*** **by G. Placidi, M. Alecci, and A. Sotgiu. Universita' dell'Aquila. (200)**

C ***Regional Nitroxide Free Radical Imaging by Low Frequency (280 MHz) EPR Spectroscopy in Whole Rat,*** **by Antonello Sotgiu. Marcello Alecci, Marco Ferrari, Valentina Quaresima, and Cinzia L. Ursini, Universita' dell'Aquila. (201)**

D ***Time-Resolved EPR Study of the Photoexcited Triplet State of CQQ Adsorbed on Silica Gel,*** **by Carlos A. Steren. Hans van Willigen, and Marco Fanciulli, University of Massachusetts at Boston and Aarhus University. (202)**

C ***Distortion of EPR Spectra Due to Materials with High Dielectric Loss,*** **by Minora Sueki. George A. Rinard, Gareth R. Eaton, and Sandra S. Eaton, University of Denver. (203)**

D *In vivo Detection of Drug Releasing Processes in Implanted Polymers by Low Frequency EPR Spectroscopy,* by Karsten Made, Bernard Gallez, Jim Liu, and Harold M. Swartz. Dartmouth Medical School. (204)

C *Enzymatic Activity of Glyceraldehyde-3-phosphate Dehydrogenase is Correlated with the Number of Active Centers Utilized Within the Tetramer,* by Joachim Baumann, Reinhard Hensel, Pia D. Vogel, and Wolfgang E. Trommer. Universitat Kaiserslautern and Universitat Essen. (205)

D *The Ionized A-Centre and Other Di-Nitrogen Defects in Diamond,* by Owain D. Tucker. Mark E. Newton, and J. Michael Baker, University of Oxford. (206)

C *EPR Studies of Radicals in Zeolites,* by Gregory L. Turner. Patrick M. Brown, and Martin G. Bakker, U.S. Bureau of Mines and University of Alabama. (207)

D *EPR-Evidence of NO-Formation in Animal Organs under Gamma-Irradiation,* by Nina V. Voevodskaya. and Ahatoly F. Vanin, Institute of Chemical Physics, Moscow. (208)

C *Utilizing Electron Paramagnetic Resonance of the Py, Center as a Probe of Interfacial Stress in Si/Si02 Systems,* by J. T. Yount and P. M. Lenahan, Pennsylvania State University. (209)

D *An ESEEM Study of^N Coupling in Vanadyl Phthalocyanine,* by Chuanfang Zhang and Jack Peisach, Albert Einstein College of Medicine. (210)

C *Annealing Characteristics of the E' and Peroxy Radical Hole Centers in Oxygen Excess and Oxygen Deficient Vitreous Si02,* by Lin Zhang. William R. Austin and Robert G. Leisure, Colorado State University. (211)

D *Matrix Peak Suppression in ^H ENDOR of Paramagnetic Ions in Disordered Solids: Distance-Dependent Enhanced ENDOR Phase (DEEP) Spectroscopy,* by Ming Zheng and G. C. Dismukes, Princeton University. (212)

C *Pulsed EOR Studies of a New Sodide, Cs^{+} (21C7)Na~.* Kerry A. Reidy-Cedergren. James L. Dye and john L. McCracken, Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan, 48824. (413)

D *Selective Inhibiion of Lipid Peroxidation by PBN in Rat Liver Microsomes,* Hong Sang. Yashige Kotake, Coit M. DuBose and Edward G. Janzen, National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, 825 N.E. 13th Street, Oklahoma City, OK 73104. (414)

C *Anisotropy Resolved EPR.* Gustavo A. Sierra. Arthur Schweiger, and Richard R. Ernst, Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland. (415)

D *Electron Zeeman Resolved EPR,* Gustavo A. Sierra. Arthur Schweiger, and Richard R. Ernst, Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland. (416)

C ***Rates of Nitric Oxide Generation From Activated Murine Macrophages Determined by Spin Trapping,*** **Torn Tanigawa. Mari Tanigawa, Ikuko Ueno, Yashige Kotate, and Edward G. Janzen, The National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, Oklahoma City, OK 73104. (417)**

D ***Hydrophobicity Profiles Across Phospholipid Bilayer Membranes at the Interface of Gramicidin and Lipid,*** **A. Wisniewska, Institute of Molecular Biology, Jagiellonian University, Krakow, Poland, J.S. Hyde, National Biomedical ESR Center, Milwaukee, WI53226, A. Kusumi, Dept. of Pure and Applied Sciences, Tokyo University, Tokyo, Japan. (418)**

C ***Oxygen Transport Within and Across Thylakoid Membranes of Spinach Chloroplasts,*** ***A.*** **Ligeza, J.S. Hyde, and W.K. Subczynski, Institute of Molecular Biology, Jagiellonian University Krakow, Poland, National Biomedical ESR Center, Milwaukee, WI 53226. (419)**

Wednesday evening: Banquet at the University of Denver Phipps Mansion to celebrate the 50th Anniversary of EPR. Transportation will be provided. Contact G.R. or S.S. Eaton for information.

Thursday, August 4, 1994
Session IX - Kev Salikhov, presiding

8:30 Presentation of International EPR Society Silver Medal by Keith McLauchlan, President

8:35 Award address: ***Multiquantum EPR Spectroscopy with Tetrachromatic Irradiation,*** **by Woiciech Froncisz. Malgorzata Jelen, Jerzy Koziol, and Tadeusz Oles, Jagiellonian University and Medical College of Wisconsin. (213)**

9:20 ***Noise Considerations with Cryogenic Microwave Amplifiers and Q-Spoiling,*** **by James S. Hyde. S. Pfenninger, and Wojciech Froncisz, Medical College of Wisconsin. (214)**

9:50 ***Spin-Lattice Relaxation in Glasses,*** **by Jacques Pescia. Sushil K. Misra, Guy Ablart, Paul Zinson, and Delphine Vergnoux, Universite Paul Sabatier and Concordia University. (215)**

10:10 Break

10:25 ***High Frequency (139.5 GHz) Pulsed EPR,*** **by Gary J. Gerfen. Lino R. Becerra, Brendan F. Bellew, Souheil J. Inati, Dennis A. Hall, Robert G. Griffin, and David J. Singel, MIT and Harvard University. (216)**

10:45 ***Development of High Frequency ESR at the National High Magnetic Field Laboratory,*** **by Louis C. Brunei. Florida State University. (217)**

11:05 ***Very-High-Field EPR and Thermal Spin Polarization Effects.*** **Ya. S. Lebedev. N.N. Semenov, Institute of Chemical Physics, Kosygina 4, 117979 Moscow, Russia. (420)**

11:30 ***Who's Who in New Pulse Sequences for EPR Spectroscopy,*** **by M. K. Bowman. Pacific Northwest Laboratory. (218)**

12:00 Lunch

Thursday lunch and afternoon: Bruker User's Group. Please contact Dr. Arthur Heiss for information.

Financial Support from Bruker Instruments, International EPR Society, New Era Enterprises, and Wilmad Glass is gratefully acknowledged

SYMPOSIUM ON FTIR/MR/RAMAN SPECTROSCOPY

Organized by Abdul R. Chughtai

Monday, August 1 1994

Keynote Speaker:

9:00 ***Indoor Air Monitoring by FTIR,*** **P. Jaakkola, Temet Instruments OY, Asentajankatu 3,00810, Helsinki, Finland; P. Saarinen and J. Kauppinen, Department of Physics, University of Turku, SF-20500, Turku, Finland; C. T. Chaffin, T. L. Marshall, R. M. Hammaker, W. G. Fatelev, Aero-Survey, Inc., 631 Levee Drive, Manhattan, KS 66502 USA. (219)**

9:30 ***Infrared Studies of Photochemical effects in Reactions of Black Carbon,*** **Abdul R. Chughtai and Dwight M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208. (220)**

9:50 ***Poly sulfide Speciation in Alkaline Solution by Raman Spectroscopy,*** **Kirk H. Michaelian, Carolyn K. Preston. Jaroslaw Szynkarczuk, Zora Ali and Daren Sawkey, Western Research Centre, Canmet, Natural Resources Canada, P.O. Bag 1280, Devon, Alberta, Canada, TOC 1EO. (221)**

10:15 ***Hydration of Particulate Carbon,*** **Abdul R. Chughtai, Michael E. Brooks and Dwight M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208. (222)**

10:35 BREAK

10:50 ***The Chemistry of Ozone and Soot as Revealed by Infrared Spectroscopy and Ancillary Techniques,*** **Abdul R. Chughtai and Dwight M. Smith. Department of Chemistry, University of Denver, Denver, CO 80208. (223)**

11:15 ***Near Infrared Gasoline Octane Prediction in the Lab and in the Field,*** **James E. Tackett. Marathon Oil Company, P.O. Box 269, Littleton, CO 80160. (224)**

11:40 ***On-line NIR Spectroscopy of Oil Sand Slurries,*** **Waldemar I. Friesen, Carolyn K. Preston and John C. Donini, Western Research Centre, Canmet, Natural Resources Canada, P.O. Bag 1280, Devon, Alberta, Canada TOC 1EO. (225)**

12:05 LUNCH

1:30 ***A Neural Network for FT-Raman Spectral Interpretation: Robustness,*** **S. Medlin. J. Morris and R. Fifer, U. S. Army Research Laboratory, AMSRL-WT-PC, Aberdeen Proving Ground, MD 21005-5066. (226)**

1:55 ***Computer Upgrade ofFT-IR Spectrometer,*** **Robert T. Lynch. Abdul R. Chughtai and Dwight M. Smith, Unversity of Denver, 2050 E. Iliff Ave., Denver, CO 80208. (227)**

2:20 ***Choosing the Proper Internal Reflection Accessory for Your Sample,*** **W. D. Perkins. The Perkin Elmer Corporation, 2305 Bering Drive, San Jose, CA 95131. (228)**

2:45 ***Consequences of Thermal Diffusion Length in the FTIR/Photothermal Spectroscopy,*** **T. Mahmood and J. R. Schlup, Department of Chemical Engineering, Durland Hall, Kansas State Universty, Manhattan, KS 66506-5102. (229)**

3:10 ***A Feasibility Study ofNIR Spectroscopy for Determination of Aromatic and Distillate Properties in Diesel and Jet Fuels,*** **Carolyn K. Preston. S. Win Lee, Elaina F. Olsen and Waldemar Friesen, Western Research Centre, Canmet, Natural Resources Canada, P.O. Bag 1280, Devon, Alberta, Canada, TOC 1EO. (230)**

3:45 ***Matrix-Isolation of Laser Desorbed Species Utilizing a Cryogenic Trap/FTIR Interface,*** **Brvan L. Carr. Robert S. Brown, Utah State University, Dept. of Chemistry and Biochemistry, Logan, Utah 84322. (231)**

SYMPOSIUM ON LUMINESCENCE

Organized by DeLyle Eastwood and Robert J. Hurtubise

Monday, August 1, 1994

Robert J. Hurtubise, Presiding

8:55 ***Opening Remarks***

9:00 ***Solid-Matrix Luminescence Properties of Benzo(a)Pyrene-DNA Adducts and Their Hydrolysis Products,*** **by R.J. Hurtubise. J.S. Corley, Y. Chu, L. Shu and S.W. Tjioe, Department of Chemistry, University of Wyoming, Laramie, WY 82071. (232)**

9:25 ***Fluorescence Energy Transfer Measurements of Rhodopsin Photostates Trapped in Trehalose Films,*** **by Sharon Sikora and T. Gregory Dewey, Department of Chemistry, University of Denver, Denver, CO 80208. (233)**

9:50 ***Solid-Phase Extraction and Solid-Matrix Luminescence as an Analytical Tool,*** **by Jie Chen and Robert J. Hurtubise, University of Wyoming Department of Chemistry, Laramie, WY 82071. (234)**

10:15 BREAK

10:30 Keynote Speaker

Approaches Towards High-Speed DNA Sequencing by Using Capillary Electrophoresis, **by Edward S. Yeung. John A. Taylor, Kyoji Ueno, Xiandan Lu, and Qingbo Li, Department of Chemistry and Ames Laboratory-USDOE, Iowa State University, Ames, IA 50011. (235)**

11:00 ***Fluorescence Studies of Surface Binding, Heterogeneity, and Migration ofSiloxane Ligands on Silica,*** **by H. Wang and J.M. Harris. Department of Chemistry, University of Utah, Salt Lake City, UT 84112. (236)**

11:30 ***Luminescence Based Oxygen Sensors,*** **by J.N. Demas and Wenying Xu, Department of Chemistry, University of Virginia, Charlottesville, VA 22901 and B.A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807. (237)**

Noon LUNCH

DeLyle Eastwood, Presiding

2:00 ***Environmental Analysis via Tunable Laser Induced Fluorescence Spectroscopy,*** **Gregory D. Gillispie and Randy W. St. Germain, Department of Chemistry, North Dakota State University, Fargo, ND 58105. (238)**

2:30 ***Evaluation of Fluorescence Excitation-Emission Matrices for Identification of Real World Oil Spills,*** **by Martha S. Hendrick. USCG Marine Safety Laboratories, Groton, CT 06340; James D. Stuart, University of Connecticut, Storrs, CT 06269; Richard B. Gaines, USCG Academy, New London, CT 06320. (239)**

3:00 ***Total Fluorescence Spectral and Lifetime Analysis of Aluminum Binding by a Commercial Humic Acid,*** **by Charles M. Sharpless and Linda McGown, Duke University, P.M. Gross Chemical Laboratory, P.O. Box 90348, NC 27708-0348. (240)**

3:30 BREAK

3:45 ***Total Fluorescence Lifetime Characterization of Complex Samples,*** **by Sherry L. Hemmingsen. Jeremy M. Shaver and Linda B. McGown, Duke University, P.M. Gross Chemical Laboratory, P.O. Box 90348, Durham, NC 27708-0348. (241)**

4:10 ***Solid-Matrix Luminescence from Trace Organic Components in Glasses Prepared from Sugars,*** **by Jiangshan Wang and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071. (242)**

4:35 ***Determination of Toxic Metal Ions Using Optical Fiber Metal Probes and Near-Infrared Compounds,*** **by Guillermo A. Casay. Dai Dong and Gabor Patonay, Department of Chemistry, Georgia State University, University Plaza, Atlanta, GA 30303. (243)**

Tuesday, August 2, 1994

Robert J. Hurtubise, Presiding

8:55 ***Opening Remarks***

9:00 ***Relationships Between the Heat Capacities of Solid-Matrices and the Luminescence Parameters of Adsorbed Phosphors,*** **by S.M. Ramasamy and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071. (244)**

9:25 ***Thermal and Optical Properties of Amorphous Metal Complexes of Mono and Dicarboxylic Acids,*** **by Richard S. Turk and Joel I. Dulebohn, Michigan Biotechnology Institute, 3900 Collins Rd., Lansing, MI 48909. (245)**

9:50 ***X-Ray Induced Luminescence in Vitreous SIO2,*** **by Allen J. Miller and Robert G. Leisure, Department of Physics, Colorado State University, Fort Collins, CO 80532. (246)**

10:15 BREAK

10:30 ***A Spectroscopic Study of Photodegradation of Ethylene-Vinyl Acetate (EVA) Copolymer Encapsulantfor PV Modules,*** **by F.J. Pern. National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401. (247)**

10:55 ***Luminescence Studies of the Metal-Carbon Multiple Bond in PhCOs(NHj)^,*** **by Scott Trammell. L. Mark Hodges, W. Dean Harman, and B. Patrick Sullivan, Department of Chemistry, University of Wyoming, Laramie, WY 82071. (248)**

11:20 ***Luminescence as a Probe for Studying Photoinduced Electron Transfer with Peptides as Intervening Media,*** **by L.E. Peitersen and B. Patrick Sullivan, Department of Chemistry, University of Wyoming, Laramie, Wy 82071. (249)**

SYMPOSIUM ON MASS SPECTROMETRY

Organized by Joseph Zirrolli

Monday, August 1, 1994

8:55 Opening Remarks: J. Zirrolli

9:00 ***Micro-Electrospray Mass Spectrometry: Ultra-High Sensitivity for Measuring Endogenous Bioactive Compounds,*** **Richard M. Caprioli. Professor of Biochemistry & Molecular Biology, University of Texas Health Science Center, Houston, Texas, 77225. (250)**

10:00 ***Matrix Assisted Laser Desorption: How "Soft" an Ionization Process?*** **.Robert S. Brown, and John J. Lennon, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300.(251)**

10:15 ***Detection of Volatile Organic Compounds in Air and Water Samples by APCITOFMS,*** **Alex F. Schreiner. Chung Hang Sin and Jon W. Carnahan, Department of Chemistry, Northern Illinois University, DeKalb, Illimos 60115. (252)**

10:30 Break & Exhibition

11:00 ***Evaluation of a Mobile Quadrupole Ion Trap Mass Spectrometer (CBMS) Designed for Detection of Microorganisms in the Environment,*** **Curtis D. Mo wry. Franco Basile and Kent J. Voorhees, Department of Chemistry, Colorado School of Mines, Golden, Colorado, 80401. (253)**

11:15 ***Gas Phase Chemistry of Simple Boron Ions,*** **Joseph Hankin. Department of Chemistry & Biochemistry, University of Colorado, Boulder, Colorado 80309. (254)**

11:30 ***Poly cyclic Aromatic Hydrocarbons: From the Laboratory to Interstellar Space,*** **Christopher Hadad. Department of Chemistry & Biochemistry, University of Colorado, Boulder, Colorado 80309. (255)**

11:45 Lunch & Exhibition

1:15 ***Measurement of Long-Chain Fatty Acyl Coenzyme A by GC/MS,*** **Keith L. Clay, and Christopher A. Johnson, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, Denver, Colorado, 80206. (256)**

1:30 ***Differentiation of Microorganisms by Pyrolysis Mass Spectrometry and Pattern Recognition of Fatty Acid Methyl Ester Extracts,*** **Franco Basile. Ted L. Hadfield and Kent J. Voorhees, Department of Chemistry, Colorado School of Mines, Golden, Colorado, 80401. (257)**

1:45 ***Analysis of Beeswax by Pyrolysis Mass Spectrometry,*** **Michael B. Beverly. Paul T. Kay and Kent J. Voorhees, Department of Chemistry, Colorado School of Mines, Golden, Colorado, 80401. (258)**

2:00 ***Identification of Lipid Metabolites from Human Eosinophib by Mass Spectrometry,*** **Denise K. MacMillan and Robert C. Murphy, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, Denver, Colorado, 80206. (259)**

2:15 ***Collision Induced Decomposition of Oxidized Phospholipids,*** **Kathleen A. Harrison and Robert C. Murphy, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, Denver, Colorado, 80206. (260)**

2:30-3:00 Break & Exhibit

3:00 ***Pyrolysis Mass Spectrometry ofGlycyl Dipeptidesj Steric and Electronic Effects on Thermal Cyclizations,*** **Alan Hendricker. B. Murugaverl and Kent J. Voorhees, Department of Chemistry, Colorado School of Mines, Golden, Colorado, 80401. (261)**

3:15 **Gas *Phase Reactions of Sila-Carbonyl Anions,* Robert Damrauer. Department of Chemistry, University of Colorado, Denver, Colorado, 80217. (262)**

3:30 ***The Sjy2 Mechanism: From Gas Phase to Solution,*** **Gustavo Davico, Department of Chemistry & Biochemistry, University of Colorado, Boulder, Colorado 80309. (263)**

3:45 ***CaCl and High Precision Measurements,*** **E. Craig Simmons. Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado, 80401 and Kathleen R. Simmons, U.S. Geological Survey, Federal Center, Denver, Colorado, 80225. (264)**

4:00 ***Stable Isotope Tracers - Advantages over Radiotracers,*** **E. Craig Simmons. Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado, 80401. (265)**

5:00 Exhibition

SYMPOSIUM ON NMR

Organized by R. E. Botto, J. R. Garbow, B. C. Gerstein, J. A. Reimer, H. Thomann, A. J. Vega, R. A. Wind, and J. P. Yesinowski

Sponsorship of this Symposium by: Bruker Instruments, Chemagnetics/Otsuka Electronics, Doty Scientific, du Pont, Isotec, JEOL USA, Monsanto, PTS, Tecmag, and Varian is gratefully acknowledged.

Monday Morning. August 1. 1994

POLYMERS

Joel R. Garbow, Presiding

8:10 WELCOMING REMARKS, Robert E. Botto

8:15 ***Characterization of Absorbed Water in Perdeuterated Polycarbonate by Residual-Proton NMR,*** **Patricia Lani Lee, and Jacob Schaefer, Department of Chemistry, Washington University, St Louis, MO 63130. (421)**

8:45 ***Xenon NMR in Polymers,*** **J. B. Miller. C. M. Roland, J. H. Walton, and J. M. Snowel, Code 6122, Chemistry Division, Navel Research Laboratory, Washington, D.C. 20375-5342. (266)**

9:15 ***Characterizing Surface Polymers with NMR,*** **J. P. Burgess, Research Triangle Institute, Research Triangle Park, NC 27709; and E. O. Steiskal. Department of Chemistry, Box 8204, North Carolina State University, Raleigh, NC 27695-8204. (267)**

9:45 ***Spatially Resolved Determination of Materials Properties by NMR-Imaging,*** **W. Kuhn. S. Hafner, P. Barth, Fraunhofer Institute for Biomedical Engineering, Magnetic Resonance Division, Ensheimer Str. 48, D-66386 St. Ingbert, Germany; P. Denner, Hochschule Erfurt, Nordhauser Str. 29, Erfurt, Germany; and S. Simon, Varian GmbH, Alsfelder Str., Darmstadt, Germany. (268)**

10:15 BREAK

10:30 ***NMR Studies of Structure and Dynamics in Macromolecular Solids,*** **Bradley F. Chmelka, Ali Firouzi. Manfred Wilheim, Heather Maynard, and Sean Williams, Department of Chemical and Nuclear Engineering, University of California, Santa Barbara, CA 93106. (269)**

11:00 ***Strategies for the Studies of Non-Crystalline Synthetic and Bio-Polymers by Solid-State NMR and Atomic Force Microscopy,*** **Tomasz Kowalewski and Jacob Schaefer, Department of Chemistry, Washington University, St. Louis, MO 63130. (270)**

11:30 ***Rotating Frame NMR Microscopy,*** **Klaus Woelk. Jerome W. Rathke, and Robert J. Klingler, Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439. (271)**

12:00 LUNCH

Monday Afternoon. August 1. 1994

BIOSYSTEMS

Robert A. Wind, Presiding

1:30 ***Decrypting the Chemical Shift Code in Proteins: A Quantum Chemical Approach to Structure in Solids and Liquids,*** **Eric Oldfield. Angel C. de Dios, Hongbiao Le, John G. Pearson, and Chenyang Lian, Department of Chemistry, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, IL 61801. (272)**

2:00 ***Recent Progress in ^^Cd NMR of Biological Systems...Model Compounds, Hemoglobin, and Fun & Games with Bones,*** **Paul D. Ellis. Andrew S. Lipton, Kate McAteer, Breege A. Concannon, Scott Mason, Roy Wuthier, Dan Reger, Rodolfo Santos, and Robert A. Wind, Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352; and Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208. (273)**

2:30 ***Photochemically Induced Dynamic Nuclear Polarization in Solid State NMR Spectra of Reaction Centers from Photosynthetic Bacteria,*** **Martin Zysmilich and Ann McDermott. Department of Chemistry, Columbia University, New York, NY 10027. (274)**

3:00 BREAK

3:30 ***Solid State NMR Studies of Nucleic Acids,*** **D. Gregory, J. Chang, D. Mitchell, S. Kiihne, J. Callahan, and G. Drobny. Department of Chemistry, University of Washington, Seattle, WA 98195. (275)**

4:00 ***Proton NMR Study of Seeds,*** **Cynthia F. Ridenour and Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.(276)**

4:30 ***Exchange Processes in Organic Crystals: Can the Solid-State NMR and Diffraction Results be Reconciled?,*** **Lucio Frydman. Department of Chemistry (M/C 111), University of Illinois at Chicago, Chicago, IL 60607.(277)**

5:00 ***Dipolar Recoupling in Solids under Magic Angle Spinning in the Spin-Locking Frame (DRAMSL),*** **B.-O. Sun. P. R. Costa, D. Kocisko, P. T. Lansbury Jr., and R. G. Griffin, Francis Bitter National Magnet Laboratory and Chemistry Department, MIT, Cambridge, MA 02139. (278)**

Tuesday. Morning. August 2, 1994

R. W. VAUGHAN LECTURE SYMPOSIUM

Robert E. Botto, Presiding

8:25 **R. W. Vaughan Lecture -** ***Population Transfer Applied to the Indirect Observation of Nuclear Spins with Large Quadrupole Coupling Constants,*** **Alexander J. Vega. DuPont Central Research and Development, P.O. Box 80356, Wilmington, DE 19880-0356; and Clare P. Grey, Department of Chemistry, State University of New York, Stony Brook, NY 11794-3400. (279)**

9:30 ***Surfaces, Solids and Gases: The Phases of NMR Spectroscopy,*** **Cecil Dybowski. Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716. (280)**

10:15 BREAK

10:45 ***Intermediate Range Order in Glasses: A New Frontier for Solid-State NMR Spectroscopy,*** **Hellmut Eckert. Department of Chemistry, University of California, Santa Barbara, CA 93106. (281)**

11:30 ***Spins, Light, Molecules, and Cats,*** **Alexander Pines. Lawrence Berkeley Laboratory and University of California, Berkeley, CA 94720.(282)**

12:15 LUNCH

Tuesday. Afternoon. August 2. 1994

POSTER SESSION

Robert E. Botto, Presiding

2:00 - 4:00 p.m.

Proton and ^C NMR Characterization of Morphology and Dynamics of Polymers, **Jolanta M. Snowel and Joel B. Miller, Code 6122, Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375-5342. (283)**

High-Resolution Solid-State NMR of Spin 3/2 Nuclei, **B. C. Gerstein. Ames Laboratory, 299 Spedding Hall, Iowa State University, Ames, IA 50011-3020. (284)**

Analysis of Electric Field Gradients and Electronic Shielding by Simulation of Spinning Sideband Intensities in M.A.S. NMR Spectra, **P. Bodart. C. Fernandez, and J. P. Amoureux, Laboratoire de Dynamique ,t Structure des Materiaux, CNRS URA 801, Universite des Sciences et Techniques de Lille, F-59655 Villeneuve d'Ascq, France. (285)**

Progress in NMR Spectroelectrochemistry, **K. Franaszczuk, A. Wieckowski. B. Montez, and E. Oldfield, Department of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Mathews Avenue, Urbana, IL 61801-3792. (286)**

Temperature-Jump MAS Experiments with a Laser Heater, **David Ferguson, Tom Krawietz, and J. F. Haw, Department of Chemistry, Texas A&M University, College Station, TX 77843. (287)**

Reconsideration of Theory of Paramagnetic Shift for Ni(II) and Co(II) in Octahedral and Tetrahedral Symmetries, **Bruce R. McGarvey. Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, N9B 3P4, Canada. (288)**

31P NMR Study of the Reaction of PMej with Mo(CO)^ in Y Zeolite, **Sanlin Hu and Tom Apple. Chemistry Department, Rensselaer Polytechnic Institute, Troy, NY 12180. (289)**

Comparison of the Solution Conformation and Histidine PKA's of fi-Amyloid Peptide Fragments, **Cynthia K. Larive and Shana L. Zink, Department of Chemistry and Center for Bioanalytical Research, University of Kansas, Lawrence, KA 66045. (290)**

Frequency-Selective Observation of Weak Heteronuclear Dipolar Couplings in Solids, **Andrew E. Bennett, Lino R. Becerra, and Robert G. Griffin, Francis Bitter National Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139. (291)**

The Use of Chemical Shift Tensors to Study Crystalline Effects in Polycyclic Aromatic Hydrocarbons, **R. J. Iuliucci. Cu Phung, Julio C. Facelli, and David M. Grant, Department of Chemistry, University of Utah, Salt Lake City, UT 84112. (292)**

^Li NMR Chemical Shifts and Li Coordination in Lithium Silicates and Aluminosilicates, **Zhi Xu and Jonathan F. Stebbins, Department of Geology and Environmental Sciences, Stanford University, Stanford, CA 94305. (293)**

Magnetic Susceptibility, Scattering, and the Solution Behavior of Complex Macromolecular Systems, **George D. Cody and Robert E. Botto, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439. (294)**

The Characterization of Lewis Acidity and Surface Aluminum in Various Aluminas and Zeolites by Means of High Resolution MAS and CP/MAS 2?Al and ^N NMR, **Alexander Blumenfeld. Dominique Coster, and Jose J. Fripiat, Department of Chemistry and Laboratory for Surface Studies, P.O. Box 413, University of Wisconsin-Milwaukee, Milwaukee, WI 53201. (295)**

Probing Electronic Structure in MjMoffieg. Quadrupole Couplings Measured by NMR, **David B. Zax. Benjamin G. M. Chew, Josh H. Golden, and Francis J. DiSalvo, Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853. (296)**

Measurement of 13Q.13Q Distances in DNA Using Radio Frequency-Driven Dipolar Recoupling NMR, **David Gregory. Dan Mitchell, Jerome Shiels, and Gary Drobny, Departments of Chemistry and Physics, University of Washington, Seattle, WA 98195. (297)**

High Frequency (139.5 GHz) Dynamic Nuclear Polarization Solid State NMR (DNP-SSNMR), **Lino R. Becerra. Gary J. Gerfen, Brendan F. Bellew, Dennis A. Hall, Robert G. Griffin, Francis Bitter National Magnet Laboratory, MIT; Richard J. Temkin, Plasma Fusion Center, MIT, Cambridge, MA 02139; and David J. Singel, Department of Chemistry, Harvard University, Cambridge, MA 02138. (298)**

Solid State NMR Studies of Self-Assembled Monolayers (SAMs), **Glen E. Fryxell, Li-Oiong Wang. John C. Lineham, and Peter C. Rieke, Battelle, Pacific Northwest Laboratories, P.O. Box 999, Richland, WA 99352. (299)**

Variable Effective Field Cross-Polarization: An Approach to Broadband Hartmann-Hahn Matching in Magic-Angle Spinning NMR, **Andrew C. Kolbert and Shervl L. Gann. Materials Sciences Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, CA 94720. (300)**

Variable-Temperature ^{13}C CP/MAS NMR Study ofFluxional Behavior of Cp^M (M=Zr, Hf, Sn) in the Solid State, **Eric J. Munson. Susan M. Paul, Marcia A. Ziegeweid, Alex Pines, Materials Sciences Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, CA 94720; and Leo Phillips, Frances Separovic, Department of Biochemistry, University of Sydney, NSW 2006, Australia. (301)**

31P NMR ofZnGePp An Optical Parametric Oscillator, **Margaret H. Rakowsky and Robert A. Mantz, The Frank J. Seiler Research Laboratory, USAF Academy, CO 80840-6272; and Phillips Laboratory, Edward AFB, CA 93524-7068. (302)**

Magnetic Effects in Bimolecular Reactions of Ion-Radicals in Solutions, **Nikolai V. Shokhirev. University of Arizona, Tucson, AZ 85721; Anatoli A. Zharikov, Institute of Chemical Kinetics and Combustion, Novosibirsk, 630090, Russia; and Eugeni B. Krissinel', Institute for Water and Environmental Problems, Barnaul, 656099, Russia. (303)**

Characterization of Gasoline Engine Combustion Chamber, Intake Valve, and Crankcase Deposits by Solid-State ^{13}C CP/MAS NMR Spectroscopy, **John C. Edwards. Texaco Research Center, P.O. Box 509, Beacon, NY 12508. (304)**

Measuring Variable-Temperature Performance of MAS Probes, **Anthony Bielecki and Douglas P. Burum, Bruker Instruments, Inc., Billerica, MA 01821. (305)**

Olefin Rotation Dynamics of Rhodium Complexes, ***Greta*** **L. Garner, Les G. Buder, Stephanie A. Vierkotter, and Craig E. Barnes, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803; and Department of Chemistry, University of Tennessee, Knoxville, TN 37996. (306)**

Field Cycling l^N NQR Imaging and Spectroscopy, **Youngil Lee and Les Butler, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803. (307)**

Solid State ^{19}F-^{13}C CP/MAS ^{13}C NMR Study of Polyfluorinated CQQ, **E. W. Hagaman and A. Gakh, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6201. (308)**

Scotch Tape, Capillary Tubing, and Superglue: High Pressure NMR, **John C. Linehan. Clement R. Yonker, James A. Franz, and Thomas S. Zemanian, Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352. (309)**

13c CPMAS and Rotational Echo NMR Studies and X-ray Crystallography of Bis-Phenols and polycarbonates, **J. B. Grutzner. B. Cowans, and Y.-H. Lee, Departments of Chemistry and Chemical Engineering, Purdue University, West Lafayette, IN 47907-1393. (310)**

Characterization of Absorbed Water in Perdeuterated Polycarbonate by Residual-Proton NMR, **Patricia Tani Lee and Jacob Schaefer, Department of Chemistry, Washington University, St. Louis, MO 63130.(311)**

Molecular Dynamics of Semisynthetic Cytochrome C; Implications for Electron Transfer, **Sheri A. Hunt. Regitze R. Void, Ph.D. and David N. Hendrickson, PH.D., Department of Chemistry, University of California, LaJolla, CA 92093. (422)**

Multi-Magnetic Resonance Studies ofNOx Reduction Catalysts, **Craig D. Hughes and William L. Earl, Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545. (312)**

Advances in Understanding ™Xe NMR in Restricted Spaces, **Yong-Wah Kim and William L. Earl, Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545.(313)**

Recent Developments in Distance Measurement Techniques for Solid State DNA Samples, **John A. Stringer, John Callahan, and Gary P. Drobny, University of Washington, Seattle, WA 98195.(314)**

Solid State NMR Structural Studies of an Intercalating Drug Bound to DNA, **Suzanne R. Kiihne. Gary P. Drobny, University of Washington, Seattle, WA 98107. (315)**

NMR, MRI, and Tumor Formation, **Rodolfo A. Santos. Darrell R. Fisher, Kevin M. Groch, Robert A. Wind, Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352; and Breege A. Concannon, Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208. (316)**

Electron Spin Echo Spectroscopy of Gamma-Irradiated Quartz, **V. V. Kurchev, Department of Chemistry, University of Houston, Houston, TX 77204-5641; and H. A. Buckmaster. Department of Electrical and Computer Engineering, University of Victoria, P.O. Box 3055, Victoria, B.C., V8W 3P6, Canada. (317)**

Phase-Cycled, Multiple-Window-Acquisition, Multiple-Pulse NMR Spectroscopy, **Thomas Barbara and Lai ma Baltusis. Varian, NMR Instrument Division, 3120 Hansen Way, Palo Alto, CA 94304. (318)**

Investigation of the Interfacial Structure of Polyphosphazene-Phosphate Molecular Composites Using 31p-Solid NMR, **William D. Samuels. Li-Qiong Wang, and Gregory J. Exarhos, Pacific Northwest Laboratory, MS: K2-44, Richland, WA 99352; and Alma R. Rodriquez, UTEP, Student Internship at Pacific Northwest Laboratory, MS: K2-44, Richland, WA 99352.(319)**

Solid-State NMR Studies ofHydroxyl Groups in Dealuminated VSYZeolites, **E. F. Rakiewicz and A. W. Peters, W. R. Grace Co., 7379 Route 32, Columbia, MD 21044; and K. T. Mueller, Department of Chemistry, Pennsylvania State University, University Park, PA 16802. (320)**

Dynamics of Methane and Ethylene Molecules on Silica Support, **Son-Jong Hwang. B. C. Gerstein, and Marek Pruski, Department of Chemistry and Ames Laboratory, Iowa State University, Ames, IA 50011. (321)**

Line Broadening and Relaxation in Molecules Adsorbed in Faujasites - A Case Study of 1-Butene, **Uwe Schwerk and Marek Pruski, Ames Laboratory, 230 Spedding Hall, Ames, IA 50011. (322)**

Quality Control in Parameter-Selective Image Analysis, **Richard Muller, Peter Barth, and Winifred Kuhn, Fraunhofer Institut Fur Biomedizinische Technik, Ensheimer Str. 48, 66386 St. Ingbert, Germany. (423)**

Tuesday Evening. August 2. 1994

GENERAL

Alexander J. Vega, Presiding

6:30 ***Solid-State NMR Studies of Isolated Two-Spin Systems Involving Nitrogen: Diazo Compounds,*** **Robin Challoner and Robin K. Harris. Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England. (323)**

7:00 ***Nuclear Quadrupole Resonance (NQR) Studies of Glass Structure,*** **Philip J. Bray. Department of Physics, Brown University, Providence, RI 02912. (324)**

7:30 ***Field Swept NMR Spectroscopy: Applications to Zeolites,*** **Xiao Wu and Les G. Butler. Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803. (325)**

8:00 - 9:30 VENDOR POSTER SESSION

Wednesday Morning. August 3. 1994

NMR/EPR

Hans Thomann, Presiding

8:30 ***Dynamic Nuclear Polarization and Electron Paramagnetic Resonance at 140 GHz,*** **L. R. Becerra, G. Gerfen, J. Bryant, B. F. Bellew, D. Hall, S. Inati, and R. G. Griffin. Francis Bitter National Magnet Laboratory, Department of Chemistry, MIT, Cambridge, MA 02139; K. J. Kreischer and R. J. Temkin, Plasma Fusion Center, MIT, Cambridge, MA 02139; and D. J. Singel, Department of Chemistry, Harvard University, Cambridge, MA 02138. (326)**

9:00 ***Pulsed ENDOR Spectroscopy of ^Fe Containing Zeolites,*** **D. Goldfarb. Chemical Physics Department, Weizmann Institute of Science, Rehovot 76100, Israel; M. Bernardo, K. G. Strohmaier, and D. E. W. Vaughan, Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, NJ 08801. (327)**

9:30 ***Dynamic Nuclear Polarization of Solvent Nuclei in Solutions Containing Free Radicals,*** **R. D. Bates, Jr.. Department of Chemistry, Georgetown University, Washington, D.C. 20057. (328)**

10:00 BREAK

10:30 ***A 29si Dynamic Nuclear Polarization/Magic Angle Spinning Study of the Silica Surface,*** **Junii Kobayashi. Materials and Electronic Devices Laboratory, Mitsubishi Electric Corp., Hyogo 662, Japan. (329)**

11:00 ***Advances and New Application in High-Frequency Pulsed EPR and Pulsed ENDOR Spectroscopy,*** **J. Schmidt. Huygens Laboratory, University of Leiden, The Netherlands. (330)**

11:30 ***Solid-State NMR and Pulsed Electron Nuclear Multiple Quantum Spectroscopic Studies of Fullerene Polymer Interfaces,*** **M. Afeworki, M. Bernardo, and H. Thomann. Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, NJ 08801.(331)**

12:00 LUNCH

Wednesday Afternoon. August 3. 1994

SURFACES/INTERFACES

Jeff Reimer, Presiding

1:30 ***Structure and Dynamics in some Low-Dimensional Composite Phases,*** **David B. Zax. Benjamin G. M. Chew and Shan Wong, Department of Chemistry, Cornell University, Ithaca, NY 14853. (332)**

2:00 ***Multi-Nuclear NMR Studies of Zeolite Ferrierite,*** **Lucy M. Bull and Anthony K. Cheetham, Materials Department, Scott J. Weigel, Chemistry Department, and Michael T. Janicke, Chemical Engineering Department, University of California, Santa Barbara, CA 93106. (333)**

2:30 ***Proton and ^p NMR of Solid Then Films and Interfaces,*** **David H. Levy, Bruce E. Scruggs and Karen K. Gleason. Department of Chemical Engineering, MIT, Cambridge, MA 02139.(334)**

3:00 BREAK

3:30 ***Connectivities from NMR Spectrometry of Solids. Applications to Materials Research,*** **Karl T. Mueller and Thomas P. Jarvie, Department of Chemistry, Pennsylvania State University, University Park, PA 16802. (335)**

4:00 ***Dynamics of Surface Adsorbed Polymers,*** **Frank D. Blum. Department of Chemistry and Materials Research Center, University of Missouri-Rolla, Rolla, MO 65401. (336)**

4:30 ***New Developments in NMR Studies of Solids and Surfaces,*** **Eric J. Munson. Marcia A. Ziegeweid, YiQiao Song, Bin He, Tanja Petrass, Holly Gaede, Rebecca Taylor, and Alex Pines, Department of Chemistry, University of California, Berkeley, CA 94720; and Dinh M. TonThat and John Clarke, Department of Physics, University of California, Berkeley, CA 94720; and Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720. (337)**

5:00 ***Intermediate-Range Structural Inhomogeneities in Glasses: A Nuclear Spin-Lattice Relaxation Approach,*** **S. Sen and J. F. Stebbins, Department of Geology, Stanford University, Stanford, CA 94305.(338)**

Thursday Morning. August 4. 1994

SPIN DYNAMICS/NEW TECHNIQUES

James Yesinowski, Presiding

8:30 ***l^N-^H Level Crossing in Immobilized Proteins,*** **Scott D. Swanson. Department of Radiology, The University of Michigan, Ann Arbor, MI 48109-0553. (339)**

9:00 ***Cross Polarization Double Rotation NMR,*** **Y. Wu. W. Sun, J. T. Stephen, and L. D. Potter, Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255. (340)**

9:30 ***31p.l9p Rotational-Echo, Double-Resonance (REDOR) NMR,*** **Yong Pan. The Procter & Gamble Company, Miami Valley Laboratories, P.O. Box 398707, Cincinnati, OH 45239. (341)**

10:00 BREAK

10:30 ***Multiple Quantum Filtration and Transfer to Heteronuclei Assigns Rare-Spin Signab,*** **Raju Subramanian and Gerard S. Harbison. Department of Chemistry, University of Nebraska at Lincoln, Lincoln, NE 68588-0304. (342)**

11:00 ***High-Resolution NMR of Single Epitaxial Structures by Optical Detection,*** **John A. Marohn. Paul J. Carson, Michael A. Miller, Jack Y. Hwang, David N. Shykind, and Daniel P. Weitekamp, A. A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125. (343)**

11:30 ***VADOR: A New High-Resolution Technique for Quadrupolar Nuclei,*** **J. P. Amoureux, C. Fernandez, and P. Bodart. Laboratoire de Dynamique et Structure des Materiaux Moleculaires, CNRS URA 801, Universite des Sciences et Techniques de Lille, F-59655 Villeneuve d'Ascq, France. (344)**

SYMPOSIUM ON PHARMACEUTICAL ANALYSIS

Organized by Michael Cutrera, Robert Lantz, and Patricia Sulik

Tuesday, August 2, 1994

Morning - Patricia L. Sulik, presiding

9:00 Opening Remarks

9:05 ***Measurement ofHydroxyl Radical Formation Using Microdialysis Sampling and GCMS Quantitation,*** **Adrian W. Pike. Paul V. Fennessey, and Jim M. McKim, Department of Pediatrics, University of Colorado School of Medicine, 4200 E. 9th Ave., Denver, CO 80262. (424)**

9:30 ***Development, Validation and Transfer of Dissolution Methods,*** **Diane Peterson, Marion Merrell Dow, Inc., 10236 Marion Park Drive, Kansas City, MO 64137. (345)**

10:10 ***Micellar Improved Determination of 6-Aminopenicillanic and 7-Aminocephalosporanic Acids,*** **Natalia Iatsimirskaia. Anatoly Yatsimirsky, and Iulia Sosnovskaya, Facultad de Quimica, Universidad Nacional Autonoma de Mexico (UNAM), Mexico D.F., 04510 Mexico. (346)**

10:30 ***Chromatography as an Analytical and Quantitative Tool for the Isolation of an Anti-Cancer Drug,*** **Vishnu Vandana and Amyn S. Teja, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332. (425)**

10:50 LUNCH

Afternoon - Michael A. Cutrera, presiding

1:30 Remarks

1-35 ***Proposed Methodfor the Analysis of Solvent Impurities in Water Insoluble Bulk Pharmaceuticals,*** **by Valerie J. Naughton. Tekmar Company, 7143 E. Kemper, Cincinnati, OH 45242. (347)**

2-40 ***Characterization of Taxol Metabolites by Liquid Chromatography/Mass Spectrometry,*** **by Kellv R. Thornburg and Robert C. Hyta, Hauser Chemical Research, 5555 Airport Road, Boulder, CO 80301; Gondi N. Kumar and Thomas Walle, Department of Pharmacology, Medical University of South Carolina, Charleston, SC 29425.(348)**

3:00 ***Can Estrone and Tamoxifen Act as Mitogens for the Growth of Endometrial and Breast Cancers?,*** **AW Pike. KK Leslie, PV Fennessey, Department of Pediatrics, Department of Obstetrics and Gynecology, University of Colorado School of Medicine, 4200 E. 9th Ave., Denver, CO 80262. (430)**

3:20 BREAK

3:30 ***Pharmaceutical Method Validation — How Much and Why,*** **by Thomas Lavloff. Director, Divisionof Drug Analysis, Food & Drug Administration, 1114 Market Street, St. Louis, MO 63101.(349)**

GENERAL POSTER SESSION

Organized by Mary E. Cast

Monday, August 1, 1994 through Wednesday, August 3, 1994

Determination of Di-(2-Ethylhexyl) Phosphoric Acid (HDEHP) in Hanford Nuclear Process Waste by Derivatization GC/MS, **by Scott M. Donaldson. Jon E.Christensen. and Rolland R. Grabbe, Westinghouse Hanford Company, P.O. Box 1970 MSIN S3-31, Richland, WA 99352. (350)**

Determination of Uranium and Thorium in Titanium by Inductively Coupled Plasma Mass Spectrometry, **by Shoii Kozuka. Masaru Hayaski, and Hideki Matsunaga, Environmental Engineering Laboratory, Research and Development Center, Toshiba Corporation, 1, Komukai toshiba, Saiwai, Kawasaki 210, Japan. (351)**

Laser-excited Atomic Fluorescence Spectrometry Applied to Real Sample Analysis — Present State of the Art and Future Potential, **by Ven Cheam, Josef F. Lechner. Roland Desrosiers, and Ivan Sekerka, Environment Canada, National Water Research Institute, P.O. Box 5050, Burlington, Ontario, Canada L7R 4A6. (352)**

Photo-oxidation Reactions Based on Singlet Oxygen Photochemistry, **by Emily Hergenreter, Chris Jensen, and Robert Milofsky, Fort Lewis College, Department of Chemistry, 1000 Rim Drive, Durango, CO 81301.(353)**

Characterization of Nucleophilic Addition Products of Thiourea and N-Acetylhistidine to N-b-Alanyldopamine and N-Acetyldopamine Quinones by NMR Spectroscopy, **by Rongda Xu. Xin Huang, Thomas D. Morgan, Om Prakash, Delbert D. Mueller, Karl J. Kramer, and M. Dale Hawley, Department of Chemistry, Kansas State University, Manhattan, KS 66506. (354)**

Aldehyde-functionalized Silanes as a New Immobilization Reagent, **by Claudia Bruning. and Joseph Grobe, University of Colorado at Boulder, Department of Chemistry, Campus Box 215, Boulder, CO 80302-0215. (355)**

General Method of the Determination of Evaporation Rates for Multicomponent Solvents Containing Halogenated Compounds, **by Jimmy L. Seidel. and Linda S. Johnson, EPA-NEIC, Bldg 53, P.O. Box 25227, Denver Federal Center, Denver, CO 80225. (356)**

Chemical and Biological Effects of Gold Mine Tailings on Larder Lake, Ontario, **by Femado Rosa. Alena Mudroch, and Trefor B. Reynoldson, Aquatic Ecosystem Restoration Branch, National Water Research Institute, Environment Canada, 867 Lakeshore Rd., Burlington Ontario, Canada, L7R 4A6. (357)**

Colorimetric Determination of Selenium as Selenite or Selenate in Mineral Premixes, **by Jeffrey A. Hurlbut, Roger G. Burkepile, Philip J. Kijak, and Carolyn A. Geisler, US Food and Drug Administration, Veterinary Analytical Section, Denver Federal Center, Bldg 20, P.O. Box 25087, Denver, CO 80225-0087. (358)**

Determination of Neomycin in Animal Feed at Therapeutic and Residue Levels by Capillary Gas Chromatography; **by Susan B. Clark. Robert J. Schmid, Jeffrey A. Hurlbut, and Carolyn A. Geisler, US Food and Drug Administration, Veterinary Analytical Section, Denver Federal Center, Bldg 20, P.O. Box 25087, Denver, CO 80225-0087. (359)**

Determination of Herbicide Residues: Simazine, Atrazine, and Propazine in Catfish by High Performance Liquid Chromatography, **by David C. Holland. Robert K. Munns, Jose E. Roybal, Jeffrey A. Hurlbut, and Austin R. Long, US Food and Drug Administration, Veterinary Analytical Section, Denver Federal Center, Bldg 20, P.O. Box 25087, Denver, CO 80225-0087.(360)**

Determination ofFlumequine, Nalidixic, Oxolinic and Piromidic Acid Residues in Catfish by High Performance Liquid Chromatography-Fluorescence/UVDetector, **by Robert K. Munns, Sherri B. Turnipseed, Allen P. Pfenning, *Steven M. Plakas, Jose D. Roybal. David C. Holland, and Austin R. Long, US Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Bldg 20, P.O. Box 25087, Denver, CO 80225-0087; *FDA/Division of Seafood Research, Dauphin Island, AL 36528. (361)**

Determination of Malachite Green and Metabolite, Leucomalachite Green in Catfish (Ictalurus punctatus) **Tissue by High Pressure Liquid Chromatography with Visible Detection (LC/VIS), by Jose E. Roybal. Allen P. Pfenning, Robert K. Munns, David C. Holland, Jeffrey A. Hurlbut, and Austin R. Long, US Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Bldg 20, P.O. Box 25087, Denver, CO 80225-0087. (362)**

Determination ofFlunixin in Milk Using Liquid Chromatography with GC/MS-SIM Confirmation, **by Heidi Rupp. David C. Holland, Robert K. Munns, Sherri B. Turnipseed, and Austin R. Long, US Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Bldg 20, P.O. Box 25087, Denver, CO 80225-0087. (363)**

Angle-Resolved Photoacoustic Spectroscopy for the Study of Molecular Orientation at Dielectric Surjaces **by Susan K. Doughty and Kathy L. Rowlen, Department of Chemistry and Biochemistry, University of Colorado, Campus Box 215, Boulder, CO 80309. (364)**

A Routine Analytical Methodfor the Monitorization of Naphthalene Degradation by HRGC and HPLC, **EAiardo P. Mateus and Rui B. Ganho, Department of Environmental Sciences and Engineering, New University of Lisbon, Quinta da Torre, 2825 Monte de Caparica, Portugal. (365)**

Determination of Selenium in Natural Water by GF-AAS After Solvent Extraction Preconcentration, **Lan-Xiang Meng, V. Nanto, Mari Walls, Uno Wegelius, A. L. Makela, P. Laihonen, W. Wang and Zhi-Min Li, University of Turku, 6-14-6 Dong Da Qiao Lu, Chaoyang District, Beijing 100020, China. (366)**

Dinophysistoxin-2: A New Shellfish Toxin in Europe, **Eoin P. Carmody, Kevin J. James and Sean S. Kelly, Chemistry Department, Cork RTC, Bishopstown, Cork, Ireland. (367)**

Assessment of Chemical Plant Air Emissions on an Urban Environment, **Kevin J. James, Mary A. Stack. Cork RTC, Bishopstown, Cork, Ireland. (368)**

Determination of Halogens in a Petroleum Product by Ion Chromatography, **H.L. Tucker. P.O. Box 2009, Bldg 9995, MS-8189, Oak Ridge, TN 37831-8189. (426)**

Identification ofGentamicin by Gas Chromatography/Negative Ion Chemical Ionizaiton Mass Spectrometry, **Barbara S. Portz. US FDA, Denver Federal Center, Bldg 20, Box 25087, Denver, CO 80225-0087, Thomas M. Heinze, National Center for Toxicological Research, Jefferson, AR 72079. (427)**

SYMPOSIUM ON QUALITY ASSURANCE

Organized by William J. Shampine

Wednesday, August 3, 1994

12:55 Introductory remarks, William J. Shampine

1:00 ***A New Microwave Instrument for Rapid Solvent Extractions,*** **Todd Kierstead. Robert Revesz, CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200. (369)**

1:30 ***Good Laboratory Practices (GLPs) in the Non-Regulated Laboratory,*** **Mark J. Lehr. U.S. Environmental Protection Agency, National Enforcement Investigations Center, Bldg. 53, Denver Federal Center, P.O. Box 25227, Denver, CO 80225. (370)**

2:00 ***Partnering as a Tool for Improving Analytical Laboratory Performance,*** **Moheb M. Khalil and Terrence P. Killeen. Westinghouse Savannah River Company, Aiken, SC 29808 and George C. Greene III, and James T. Chambers, General Engineering Laboratories, Charleston, SC 29417. (371)**

2:30 ***QAING the Quality Assurance Unit,*** **William N. Palmer. U.S. EPA, NEIC, P.O. Box 25227, Denver, CO 80225. (372)**

SYMPOSIUM ON RADIOCHEMISTRY

Organized by Ann Mullin

Monday, August 1, 1994

Sponsorship of this symposium by Quantalex, Inc., Lakewood, CO is gratefully acknowledged.

Ann Mullin, presiding

8:30 **Introductory Remarks**

8:35 ***Remote Atmospheric Gamma-Ray Spectroscopy with HPGe Detectors and Satellite Data Transmission,*** **by Colin G.Sanderson, Norman Latner, and Richard Larsen, Environmental Measurements Laboratory, U.S. Department of Energy, 376 Hudson Street, New York, New York 10014-3621. (373)**

9:05 ***Possibilities and Limitations of the Use of Naturally-Occurring Sulphur-35 in Small Watersheds,*** **by R.L.Michel. J.T.Turk, and D.L.Naftz, U.S.Geological Survey, 431 National Center, Reston, Virginia 22092. (374)**

9:35 ***Statistical Process Control for Alpha Spectroscopy,*** **by William Richardson. Richard Seymour, and Ronald Majoras, Oxford Instruments Inc., Nuclear Measurements Group, 601 Oak Ridge Turnpike, Oak Ridge, Tennessee, 37830. (375)**

10:05 **BREAK**

10:30 ***Radiotracer Study of Electrode Surfaces,*** **by Maria Gamboa- Aldeco, Krzvsztof Franaszczuk. and Andrzej Wieckowski, Department of Chemistry, University of Illinois, 600 South Mathews Avenue, Urbana, Illinois, 61801. (376)**

11:00 ***Improvements in Alpha Spectrometry,*** **by Wayne P.Graves. ORDELA, Inc., 1009 Alvin Weinberg Drive, Oak Ridge, Tennessee, 37830, and W.Jack McDowell, ETRAC, Inc 1009 Alvin Weinberg Drive, Oak Ridge, Tennessee, 37830. (377)**

11:30 **LUNCH**

1:00 ***Using Geology to Predict Radon Occurrence: Scale Consideration,*** **by R.Randall Schumann. U.S.Geological Survey, MS 939, Federal Center, Denver, Colorado, 80225-0046. (378)**

1:30 ***The Nature and Timing of Uranium Uptake in Wetlands: Some Unique Perspectives Based on Radiography and Uranium Decay-Series Isotopes,*** **by Robert A.Zielinski. Charles A.Bush, and John N.Rosholt (deceased), U.S.Geological Survey, MS 974 Federal Center, Denver, Colorado, 80225-0046. (379)**

2:00 ***Plutonium-239+240 and Americium-241 in Soils East of Rocky Flats, Colorado,*** **by M.Iggy Litaor. M.L. Thompson, G.R. Barth, and P.C. Molzer, E.G.&G., Rocky Flats, Bldg 080, Golden, Colorado, 80402-0464. (380)**

2:30 **BREAK**

2:45 ***The Effects of Vegetation on Soil Gas Rn-222 Concentration and Transport,*** **by Joel Webb. Colorado State University, Fort Collins, Colorado, 80523. (381)**

3;l5 ***A Soil Monitoring System for Assessing Contaminant Transport: Plutonium-239+240 and Americium-241,*** **by M.Iggy Litaor. G.R. Barth, P.C. Molqer, E.M. Zika, H. Daniels, and J. Moffitt, E.G.&G., Rocky Flats, Bldg. 080, Golden, Colorado, 80402-0464. (382)**

3:45 ***C-14 Transport at Yucca Mountain,*** **by Donald C.Thorstenson U.S.Geological Survey, MS 418, Federal Center, Denver, Colorado, 80225-0046. (383)**

Tuesday, August 2, 1994

Sponsorship of this symposium by Oxford Instruments, Inc., Nuclear Measurements Group is gratefully acknowledged.

8:30 Panel Discussion

"Do Laboratory Audits Lead to Improved Data Quality?"

Moderator: Colin Sanderson, U.S.Department of Energy, EML
Panel Members: David McCurdy, Yankee Atomic Electric Co.
J.S.Morton, U.S.Department of Energy, RESL
Paul Hahn, U.S.Environmental Protection Agency, EMSL
Karen Schoendaller, E.G.&G., Rocky Flats
James Harvey, International Technology Corporation
Daniel Montgomery, Analytics, Inc.

11:30 LUNCH

1:00 ***Quality Assurance for Radiological Emergency Response Field Laboratories,*** **by Paul Hahn. U.S. Environmental Protection Agency, P.O. Box 93478, Las Vegas, Nevada, 89193-3478.(384)**

1:30 ***The In-House Continuing Education Program for Technical Staff at an Analytical Services Laboratory,*** **by James R.Noyce and Mathias M. Lardy, International Technology Analytical Services, 2800 George Washington Way, Richland, Washington, 99352. (385)**

2:00 ***Emerging Issues in Automated Environmental Radiochemistry Data Verification, Validation, and Assessment,*** **by Keith A.Wegner. Steven A Ziliak, Gregg A.Starkel, David W.Moody, and David M.Etzel, QuantaLex, Inc., 300 Union Boulevard, Suite 600, Lakewood, Colorado, 80228. (386)**

2:45 BREAK

3:00 ***Experience with Performance Specifications for Some Radiochemical Analyses,*** **by Carl T.Bishop. FERMCO, P.O. Box 398704, Cincinnati, Ohio, 45239. (387)**

3:30 ***The ASTM Process for Radioanalytical Methods in Water*** **by James T. Harvey. IT Corporation, 9000 Executive Park Drive, Suite A-110, Knoxville, Tennessee 37923.(388)**

4:00 ***Screening of Radioactive Samples for Purposes of Inventory*** **by Terry T.McKibbin. ENSECO, Rocky Mountain Analytical Laboratory, 4955 Yarrow Street, Arvada, Colorado, 80002. (389)**

Wednesday, August 3, 1994

8:30 ***Radon in Water at Public Supply Systems Well heads or Entry Points,*** **by Loren Berge. Scientific Laboratory Division, Department of Health, State of New Mexico, 700 Camino de Salud, NE, Albuquerque, New Mexico, 87106. (390)**

9:00 ***Iron-55 Anomalies in Reactor Liquid Samples,*** **by J.S.Morton. U.S.Department of Energy, Radiological and Environmental Sciences Laboratory, 785 DOE Place, Idaho Falls, Idaho, 83401-1562. (391)**

9:30 ***Applications oflNAA (Instrumental NeutronActivojtion Analysis) to Various Matrices,*** **by James Budahn. U.S.Geological Survey, MS 974, Federal Center, Denver, Colorado, 80225 (392)**

10:00 ***Determination of Radiostrontium in Environmental Media by Cerenkov,*** **by David E.McCurdv. Yankee Atomic Electric Company, 580 Main Street, Bolton, Massachusetts, 01740. (393)**

10:30 BREAK

10:45 ***Low Level Alpha Detection by Chemical Means,*** **M.P. Neary. NUS Laboratory, 5350 Campbells Run Road, Pittsburgh, PA 15205. (394)**

11:15 ***Buying Radiochemical Analytical Services - How to Get the Most for Your Money,*** **by Marilyn J.Avers and Keith Wegner, QuantaLex, Inc., 300 Union Blvd., Suite 600, Lakewood, Colorado, 80228-1554. (395)**

11:45 ***Numerical Analysis of Convolved Alpha Spectra, ,*** **M.P. Neary. NUS Laboratory, 5350 Campbells Run Road, Pittsburgh, PA 15205. (428)**

12:15 ***Diagnosis of Gastric Cancer by (7-T)Tetracycline,*** **Zhi-Min Li, Lan-Xiang Meng, Dong Chen, Ao Yuang, CIAE, 6-14-6 Dong Da Quao Lu, Chaoyang District, Beijing 100020, China. (420)**

SYMPOSIUM ON LABORATORY SAFETY

This symposium has been cancelled.

SYMPOSIUM ON ROBOTICS

Organized by Gerald L. Hoffman

Wednesday, August 3, 1994

1:00 ***Integrated Sample Automation for Environmental, Food, and Chemical Testing.*** **Mark Cava. Zymark Corporation, Zymark Center, Hopkinton, MA 01748. (396)**

1:30 ***Ultra-Low-Cost Exploratory Robotic Construction Systems for PC's,*** **Evan Rosen. Advanced Design, Inc., 1101 East Rudasill Road, Tucson, AZ 85718. (397)**

2:00 ***An Inexpensive Articulated Arm Robot for Education and Entry Level Robotic Applications,*** **Marcraft Inc., 100 North Morain Street, Kennewick, Washington 99336, Rodney Stockton. SLR Systems, 2950 George Washington Way, Richland, WA 99352. (398)**

0.30 ***Comparison of Some Currently Available Laboratory Scale Robots,*** **Rodney Stockton. SLR Systems, 2950 George Washington Way, Richland, WA 99352. (399)**

3:00 **BREAK**

3.3O ***Robotics/LIMS Interface to a Combustion Furnace used in Conjunction with a Carbon/Sulfur Analyzer,*** **Philip J. Farrelly. Hudson Control Group, Inc., 44 Commerce Street, Springfield, NJ 07081. (400)**

4:00 ***Validating a Blood Glucose Data Acquisition System in Today's FDA Environment,*** **Aimee Scheiman, LIFESCAN, Johnson and Johnson Company, 1000 Gibraltar Drive, Milpitas, CA 95035. (401)**

4:30 ***Verification System for an Automated Screw Cap Removal Device,*** **Gerald L. Hoffman. U.S. Geological Survey, National Water Quality Laboratory, Methods Research and Development Program, 5293 Ward Road, Arvada, CO 80002. (402)**

1 NEW SOURCES AND DETECTION SYSTEMS FOR ATOMIC MASS SPECTROMETRY. **Gjry. M. Hieftie. Mark J. Heintz, Gangqiang Li, Patrick P. Mahoney, and David P. Myers, Indiana University, Department of Chemistry, Bloomington, IN 47405**

Atomic mass spectrometry, usually implemented as either ICP-mass spectrometry (ICPMS) or glow discharge mass spectrometry (GDMS), has become a commonplace method for ultratrace elemental analysis in samples of various kinds. The techniques offer unprecedented detection limits in a multielement mode, elemental coverage virtually across the periodic table, broad dynamic range, isotope-analysis capability, excellent performance in a semiquantitative mode, and only moderate levels of matrix and spectral interferences. However, the methods still suffer from a number of shortcomings, including isobaric overlap from polyatomic species, residual matrix interferences, instrumental cost and complexity, and limited precision. Furthermore, because all commercial instruments require sequential scanning of the isotopes or elements of interest, a tradeoff is usually necessary between high sensitivity and elemental (isotopic) coverage when a transient sample is analyzed. In this presentation, these shortcomings will be considered and new instrumental approaches will be described. Prominent among the sources to be examined is a new magnetically assisted radio frequency GD, that not only can be used to analyze nonconductive solids directly, but also is simpler to interface to a mass spectrometer. Novel mass spectrometers to be described are a time-of-flight system and another that couples a multichannel array detector with a double-focusing sector instrument. Importantly, both new spectrometers offer virtually simultaneous monitoring of all masses of interest.

2 A NEW TECHNOLOGY IN HIGH PERFORMANCE ICP-MS

C.B. Douthitt, Finnigan MAT, 9412 Rocky Branch Dr., Dallas, TX 75243

A compact high performance ICP-MS (the Finnigan MAT model **ELEMENT),** exclusively tailored to the characteristics of a plasma source at atmospheric pressure, has designed from first principles. The innovative analyzer design, combined with an expert mass control system offers the speed, operating convenience and front-end accessibility of a quadrupole-based ICP-MS while providing the selectivity to resolve the most common spectral interferences. The resolving power of this analyzer can be switched in one second between 300, 3000, and 7500 times that of a quadrupole analyzer. The trapezoidal peak shape, typical for magnetic sector analyzers, is of particular benefit to analysts having to perform fast high precision isotope ratio determinations. The dual mode detector with a dynamic range of more than 9 orders of magnitude, dark noise <0.2 counts/sec, and no mass discrimination allow analyses of concentrations ranging from per cent to ppq levels.

3 THE POWER OF ELEMENTAL "FINGERPRINTING" USING THE IRIS, A CID BASED ICP-AES
John E. Schmelzel and Mike Pi Ion, Thermo Jarrell Ash, 8E Forge Pkwy., Franklin, MA 02038

The IRIS is the first plasma spectrometer to view the entire emission spectrum simultaneously. The IRIS consists of an echelle optical system with a CID detector. The CID detector produces a complete 2 dimensional emission spectrum. These elemental "fingerprints" can be compared directly by image subtraction. The resulting image reveals the elemental differences between the samples. This offers a quick method for characterization of a variety of sample matrixes. This paper details the IRIS spectrometer and its application to oil-field brine samples.

4 **RELATING ELEMENTAL AND ALGAL CONSTITUENTS OF ESTUARINE WATERS THROUGH MULTIVARIATE ANALYSIS OF ICP MASS SPECTRA.** Michael E. Ketterer. Department of Chemistry, John Carroll University, University Heights, OH 44118; Jeffrey R. Johansen and Gerald V. Sgro, Department of Biology, John Carroll University, University Heights, OH 44118.

In the Great Lakes basin, widespread potential for anthropogenic impact upon aquatic ecosystems and water resources exists, particularly in estuarine areas near larger population centers. Many diverse types of measurements are useful for assessing this anthropogenic impact; the authors are examining changes in elemental compositions and algal population distributions for a number of Lake Erie estuaries located in and near Cleveland, OH. Our work compares, in the multivariate sense, information about algal parameters and elemental compositions of the ecosystems; we are using principal components analysis and canonical correspondence analysis to examine patterns therein. Of particular interest is how principal components analysis (PCA) can be directly applied to ICP mass spectral intensities of water samples without undertaking any "calibration" whatsoever, and how this intensity dataspace is essentially the same as a dataspace of "calibrated" concentrations of specific elements. Some of the interelement PC's and their relationships to the algal PC's will be discussed.

5 **DETERMINATION OF SELENIUM IN BLOOD SAMPLES BY GF-AAS.** **Lan-Xiang Meng, V.Nanto, Uno Wegelius, A.L.MMkela, W.Wang and Zhi-Min Li, University of Turku, 6-14-6 Dong Da Qiao Lu, Chaoyang District, Beijing 100020, China.**

For the selenium levels in man, blood is normally taken as indicator sample. For determination of selenium in blood samples, the principal problems are small size and its very low concentration. In order to achieve the required sensitivity the Graphite Furnace - Atomic Absorption Spectrometer (GF-AAS) has been used. Alternate digestion method with nitric acid and peroxide hydrogen was used for blood samples. After digestion, nitric acid and hydrochloric acid with different acidity were used as dissolution medium. Its acidity ranged from 0.25 - 2.5 N. The results showed that hydrochloric acid was better one as dissolution medium than nitric acid. Both acids and acidity have effect on recovery of selenium. Hydrochloric acid has wider acidity ranges, under which conditions the Se - recovery is more than 96.5 % when acidity ranges from 0.25 - 2.5 N, but nitric acid has narrow acidity range under which the selenium recovery is more than only 95.1 %. Lower acidity hydrochloric acid (0.6 N) is used as dissolution agent. Selenium in blood samples of 139 healthy medical students at the University of Turku has been determined by GF-AAS under selected conditions.

6 HIGH RESOLUTION ICP-MS FOR ULTRA TRACE ANALYSIS IN DIFFICULT MATRICES

C.B. Douthitt, Finnigan MAT, 9412 Rocky Branch Drive, Dallas, TX 75243

Spectral interferences by polyatomic or multiply-charged species are major limitations to analysts currently using quadrupole-based ICP-MS instruments. The recognized advantageous characteristics of atmospheric plasma ionization in respect to quantitative multi-element or isotopic analysis are significantly deteriorated by the limited resolving power of quadrupole analyzers, -unit resolution across the mass range. The result is poor sensitivity for many elements and lack of selectivity. Despite considerable effort was on improved sample preparation and sophisticated clean-up techniques, common interferences remain an inherent problem in elemental plasma mass spectrometry, in particular at ultra trace levels. Significant improvement has been achieved by using a double focussing magnetic sector-based high resolution analyzer instead of a quadrupole analyzer. A summary of recent analyses of biological, ceramic, and semiconductor matrices for elements whose analysis is either difficult or impossible at unit resolution will be presented.

7 DETERMINATION OF SILICON CONCENTRATIONS IN WF_6 RESIDUE SAMPLES BY THE GRAPHITE FURNACE ATOMIC ABSORPTION TECHNIQUE. **Greg W. Johnson, Bandgap Chemical Corporation, 1861 Lefthand Circle, Longmont, Colorado 80501.**

Demand for ultra high purity tungsten hexafluoride by the microelectronics industry continues to reach record levels. The standard industry method for trace metals analysis in WF_6 involves preparation of a residue sample and analysis by Inductively Coupled Plasma fJCP)-Mass Spectrometry, ICP-Atomic Emission Spectrometry, Graphite Furnace Atomic Absorption Spectrophotometry, and Flame Emission Spectrometry. Bandgap Chemical Corporation routinely provides customers with analysis of 42 trace elements, most with detection limits below 1 ppbwt. However, customer specifications are constandy evolving to reflect new industry concerns about control of contamination.

Recently, Bandgap responded to a customer request to develop a specification for silicon at <20 ppbwt in WF_6 residue samples, an element not previously included in standard trace metals analysis. A method for determination of Si was developed using GFAA. Problems associated with tungsten and fluoride were encountered in Si spike recovery experiments. Characterization of the effects of these interfering elements will be presented. The successful control of interferences by the use of a matrix modifier will be discussed.

8 Abstract Not Available

9 AN INVESTIGATION INTO THE DETECTION OF TRACE METALS IN REFACTORY SAMPLE MATRICES UTILIZING INDUCTIVELY COUPLED PLASMA CO-AXIAL VIEWING ATOMIC ABSORPTION SPECTROSCOPY. **GarvD. Ravson. Carl E. Hensman, Department of Chemistry and Biochemistry, New Mexico State University, Box 30001 Dept. 3C, Las Cruces, New Mexico. 88003**

The advantages of atomic absorption spectroscopy (AAS) compared to atomic emission spectroscopy (AES) are well understood and documented. The AES optical collection system incurs problems due to interference's from refractory elements and spectral overlapping. Refractory materials have been efficiently atomized with the application of high temperature sources, most notably the inductively coupled plasma (ICP). Unfortunately, the high energies afforded by these sources has resulted in the realization of increased atomic and ionic spectral interference's. These interference's could be significantly diminished by use of AAS as a wavelength specific detection scheme. Work has been initiated which entails a practical aspect of inductively coupled plasma atomic absorption spectroscopy (ICPAAS). Previous investigations have shown that by passing light co-axially rather than across the discharge, a substantial increase in spectral rejection and improved limits of detection can be realized. This technique involved the modulation of the rf power applied to the plasma and use of time-gated data acquisition. The utility of this approach to the detection of trace metals in refractory sample matrices which have been prone to spectral interference's will be discussed.

10 LASER VAPORIZATION WITH RESONANT EXCITATION IN ULTRA-TRACE ELEMENTAL ANALYSIS—APPLICATION TOWARDS SINGLE CELLS. **C. J. Smith and E. S. Yeung, Department of Chemistry and Ames Laboratory-USDOE, Iowa State University, Ames, IA 50011.**

Current methods used for the analysis of the contents in single cells suffer from either quantitative inaccuracy or from a slow sampling rate. Recently, using laser vaporization at prebreakdown fluences, researchers in this group have demonstrated with quantitative accuracy the rapid analysis of Na and K in red blood cells. The work discussed here focuses on the incorporation of a tunable laser source for the simultaneous laser vaporization and resonant excitation of analyte species. Since the tunable light source provides a direct means of atomic excitation, atomic fluorescence can be used in ultra-trace elemental analysis. The analyte fluorescence emitted in the vaporization plume is collected along with the acoustic signal, which is used to normalize the optical signal. Results are presented for laser vaporization of a liquid jet and the extension to a sheath-core flow cell, which is used in the single-cell analysis. The advantage of this technique is its ability to rapidly form a statistical profile of analyte variations in a population of single cells and to detect abnormal analyte contributions, which may have been averaged out in a bulk sample.

DEVELOPMENT OF AN ALTERNATIVE METHOD OF MEASURING EXCITATION TEMPERATURES INDEPENDENT OF BOLTZMAN EQUILIBRIUM ASSUMPTIONS: APPLICATIONS AND MPLICATIONS
Gary D. Rayson and Michael W. Duarte, Department of Chemistry and Bochemistry, New Mexico State University, Box 30001, Las Cruces, New Mexico, 88003

Development of an alternative method of measuring excitation temperatures in an inductively coupled plasma (ICP) is described. The argon plasma used in ICP instrumentation, exhibits non-local thermodynamic equilibrium (non-LTE) characteristics. This approach will enable the determination of this diagnostic parameter without the use of Boltzman equilibrium assumptions. This alternative method intails sinusoidal modulation of the amplitude of the applied RF power wave form and monitoring of the magnitude and the phase of the subsequent emission waveforms arising from transitions originating from specific upper energy levels of atomic argon. Data processing is based on algorithms developed for phase-resolved lifetime measurements. These "lifetimes" provide time constants indicative of the "excitation temperature" of the ICP. The application of viewing different argon emission lines and their associated upper energy levels allows an alternate means to obtain "time constants" necessary for steady state excitation temperature measurement independent of Boltzman type LTE assumptions. The application and implications of this alternate approach to temperature measurements within the analytical ICP independent of assumptions will be discussed.

Abstract Not Available

USING AN ADVANCED HIGH PRESSURE DIGESTION VESSEL AS A NEW APPROACH TO MICROWAVE SAMPLE PREPARATION OF REACTIVE SAMPLE-TYPES.
Bob Fidler. Sara Littau, CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200

Closed-vessel microwave acid digestion of samples containing high organic content has proven challenging since digestion of such materials may result in spontaneous and excessive gaseous evolution. Traditionally, microwave digestion vessels have been constructed to withstand internal pressures to 200 psi before pressure is released via built-in venting mechanisms. When an extreme over-pressurization occurs causing a vessel to vent, the sample may be lost. However, recent developments in vessel design technology offer improved capability to withstand internal pressures to over 600 psi. This proves especially valuable during digestion of samples with high or unknown levels of organic content. The vessel, constructed entirely of microwave transparent material, is protected against over-pressurization by a unique rupture membrane system designed to operate at high pressures and can be easily hand-vented upon completion of the digestion process. In-situ monitoring of both temperature and pressure inside the vessel offers the possibility to more closely control the rate of reaction. This paper will detail examples where a high pressure digestion vessel can be used more effectively for sample types not easily handled using traditional microwave digestion vessel technologies.

13 OPTIMIZATION OF PHOTODIODE ARRAY DETECTION AND HPLC MOBILE PHASES FOR DETECTION OF COELUTING IMPURITIES
Jeanne B. Li and Richard L. Cotter, Waters, Division of Millipore, 34 Maple Street, Milford, MA 01757

HPLC-photodiode array detection (PDA) technology is a powerful combination of chromatographic separation and on-line detection spectral analysis. Recent advances in PDA optics and spectral analysis software provide new analytical tools for impurity detection. The Waters™ 996 PDA with optical resolution of 1.2 nm detects spectral fine structure for differentiation of similar spectra for peak identification and analysis of peak homogeneity. Millennium™ 2010 software uses Spectral Contrast™ algorithms for mathematical assessment of spectral differences. The 1.2 nm resolution also extends the linear range of the PDA to permit good quantitative analysis over a large concentration range. Good noise performance is required for high signal-to-noise for high sensitivity to detect trace components. All of this new technology can not be employed without a good analytical method. To optimize performance, the analyst must choose the appropriate mobile phase containing components with low absorbance, since UV absorbance of the mobile phase can adversely affect both linearity and noise performance. Because spectral analyses encompass more than one wavelength, the detection of coeluting impurities requires more stringent analytical conditions than quantitation using a single wavelength. Other parameters such as wavelength range and sample amount are equally important. Illustrations of these interactions between the chemistry and the hardware; and solutions to analytical problems will be shown. With an optimized HPLC separation and the appropriate selection of mobile phase and PDA parameters, the ability to detect low concentrations of coeluting impurities with certainty increases.

14 NEW HPLC METHOD FOR THE DETERMINATION OF PEROXYACETIC ACID. **Ulrich Pinkernell, UweKarst, and Karl Cammann, Institute for Chemical and Biochemical Sensor Research, Westfalische Wilhelms-Universitat Minister, Wilhelm-Klemm-Str. 8, 48149 Munster, Germany**

Peroxyacetic acid (PAA) is a widely used disinfectant in food and beverages industry. Accurate determination of PAA in the presence of a large excess of hydrogen peroxide is necessary to control the PAA levels during disinfection processes to obtain the optimum disinfection effectivity. The most popular method for the determination of PAA is still a two-step redox titration which suffers from a low accuracy. We will describe a new HPLC method for the selective analysis of PAA in the presence of excess hydrogen peroxide. Methyl-p-tolylsulfide (MTS) is oxidized by PAA, forming the corresponding sulfoxide (MTSO). These substances can be separated easily by high performance liquid chromatography on a reversed phase column and detected by ultraviolet spectroscopy at a wavelength of 230nm. As MTSO is a commercially available solid substance, it can conveniently be used for calibration. Therefore, calibration with the unstable PAA can be avoided. Our method is characterized by a high reproducibility, low detection limits, an applicable concentration range of more than two decades and low cross reactivity towards hydrogen peroxide.

15 ANALYSIS OF NERVE AGENT DEGRADATION PRODUCTS USING CAPILLARY ION ELECTROPHORESIS. **Stuart A. Oehrle, Waters Chromatography, 34 Maple Street, Milford, MA 01757**

A method has been developed for the analysis of nerve agent degradation products using capillary ion electrophoresis. Indirect UV detection and various electrolytes were investigated. Analysis of the primary degradation products isopropyl methylphosphonic acid (IMPA), ethyl methylphosphonic acid (EMPA), and pinacolyl methylphosphonic acid (PMPA), and methylphosphonic acid (MPA) was accomplished with run times of less than five minutes. Detection of low part-per-miUion (ppm) levels of degradation products in spiked water samples was possible. Preliminary investigations have found detection limits of less than 1 ppm (mg/L) by hydrostatic injection. Sub-ppm detection levels have been found by using electromigration as an injection mode.

17 DEVELOPMENT OF A SEMI-AUTOMATED CLEAN-UP PROCEDURE FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN AMBIENT AIR SAMPLES. **Nick P. Alexandrou. Kenneth A. Brice, Environment Canada, Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ontario, M3H 5T4, Canada.**

The determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air samples (at pgm^{-3} levels) is of current concern because of the suspected toxicity of these species. Typical methods involve sampling a large volume of air (approx. $300m^3$), with collection of particulate-phase and vapour-phase PAHs on fdter and adsorbent media respectively. Following solvent extraction, the reduced volume extract must be subjected to a suitable clean-up procedure to isolate the PAHs, eliminating contamination and interferences that could complicate the final analytical procedure (usually GC-FID/MS or HPLC). This clean-up procedure is typically labour-intensive, time-consuming and subject to operator error. In this laboratory, a sample clean-up procedure using sequential silica and alumina solid-phase extraction (SPE) cartridges has been deployed in the determination of targeted individual 2-ring to 6-ring PAHs, with the final analysis being performed using HPLC and programmable fluorescence detection. In an effort to increase sample-handling capacity and improve reproducibility, automation of this clean-up procedure has been implemented using a Waters Millilab SPE Workstation. A number of commercial SPE cartridges suitable for such automated systems have been evaluated, but many have been found unacceptable for this application because of contamination arising from the cartridge body. The fractionation of PAHs from the alumina clean-up step has been found to depend critically upon the activity of the alumina batch used to pack the cartridge. Special precautions are also necessary to avoid deactivation of the alumina by ambient water vapour during storage and actual use. These difficulties have all been overcome and the procedure is now being routinely applied to the analysis of ambient samples. Consistent fractionation and good, reproducible recoveries have been achieved.

404 EXTRACTION EFFICIENCIES OF SPIKED VERSUS NATIVE PAHS FROM WET CLAY USING STANDARD METHODS AND A CLOSED EXTRACTION METHOD. Marshall D. Tilbury, Paul C. Winkler, and Donald C. Zapien, Enseco/RMAL, 4955 Yarrow Street, Arvada, Colorado 80002.

A lpptn L6 component poly aromatic hydrocarbon (PAH) homogeneously spiked wet clay was synthesized by drying, seiving, and spiking a clean wet clay which was then re-constituted with *18%* snow and brought to the original density of 2 g/cc. The raw wet clay and the dried seived clay were also spiked at lppm with the 16 component PAH mix prior to extraction. The standard extraction procedure consisted of manually dispersing the 30g matrices with sodium sulfate followed by horn sonication in methylene chloride. The extract was then dried, filtered, and concentrated via Kuderna-Danish/ N-evaporation to 1.0 ml. The alternative method devised a high sample capacity mechanical dispersion step for the 30g matrices utilizing a closed preparation system with pulsed methylene chloride and a down line concentrator equipped for solvent recovery. Results indicated the homogeneously spiked wet matrix was acheived, and this native matrix PAH recoveries were much lower than traditional PAH spiking procedural recoveries. The closed extraction system PAH recoveries were equivalent or superior to the standard extraction method's PAH recoveries.

405 EXTRACTION EFFICIENCIES AND AQUEOUS/SOLID PARTITION RATIOS OF PCBS IN SEDIMENT WATERS VIA SPE AND LLE. Marshall D. Tilbury, Paul C. Winkler, and Donald C. Zapien, Enseco/RMAL, 4955 Yarrow Street, Arvada, Colorado 80002.

One liter water samples were spiked with 5 ppb AR1254 and varying amounts of 10 um opaline silica to assimilate real water matrices. The samples were extracted at different residence intervals by way of traditional liquid/liquid extraction (LLE), as well as a novel solid phase extraction (SPE) method that enabled the extraction of the total matrix as well as providing the fractionation of the aqueous and solid matrices. Results indicated a fast aqueous/solid equilibrium time of the PCBs. It was also determined that there is a formidable PCB aqueous/solid partition coefficient (log K of 2.5) for this chosen matrix. The diminished PCB recoveries for the LLE sediment waters is attributed to this large partition ratio while the semi automated (SPE) method provided excellent PCB recoveries, proper matrix spiking procedures and method development strategies are discussed to ensure accurate experimental results.

18 MECHANISMS REGULATING COMPOSTING OF HIGH CARBON TO NITROGEN RATIO GRASS STRAW. William R. Horwath and Lloyd F. Elliott, Oregon St Univ. and USDA-ARS, 3450 SW Campus Way, Corvallis, OR 97331, (503) *750-8756.*

Utilization of high C:N ratio farm residues is difficult because of low value and bulk. Composting is an ideal method for upgrading the residue, however, it was not thought possible without co-composting. We have successfully composted grass straw with a ON ratio of 70:1 by establishing ideal bulk density and moisture regimes. After turning and densification, composting conditions are achieved with the rapid growth of thermophillic bacteria, actinomycetes and fungi. During the thermophillic phase, bacteria range from 108-109 g-l straw. Actinomycetes number 108 g-1 straw. Fungi range from 10^{6}-10^{7} propagules g^{-1} straw. Microbial biomass C during composting represents 4-6% of total straw C. A significant amount of lignin C, 25%, was degraded during mesophillic decomposition. During thermophillic decomposition, lignin C continues to decline to 60% of the initial content. The acid insoluble lignin fraction becomes highly oxidized and accumulates N. Decomposed lignin C, *N*, H, and O concentrations were similar to humic substances. Modeling of microbial production indicated that the microbial biomass was more efficient at mesophillic than at thermophillic temperatures. The study of microbial dynamics and straw biodegradation will be integrated into a low-input approach to sustain nutrient cycling in cropping systems.

19 **INOCULATION OF PURELY CULTURED THERMOPHILIC BACTERIUM, BACILLUS LICHENIFORMIS NAL, AIMED TO ACCELERATE THE ORGANIC MATTER DECOMPOSITION AT THE EARLY STAGE OF HIGH RATE COMPOSTING.** **Kivohiko Nakasaki. Nobuyuki Uehara, Minoru Kataoka, and Hiroshi Kubota, Dept. of Chemical Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432 Japan**

Composting experiments were conducted by using a laboratory scale autothermal packed bed type reactor where an uniform temperature, 60 C was maintained. And the effects of inoculation of purely cultured thermophilic bacterium, *Bacillus licheniformis* NA1 were evaluated by measuring time course of C02 evolution rate, conversion of carbon, NH3 evolution rate, pH, and microbial succession. These values differed substantially between the compostings in which the NA1 strain was inoculated or not. When the bacterium was not inoculated, the lowering of pH in the early phase caused to inhibit the activities of microorganisms and resulted in termination of the organic matter decomposition. By contrast, the NA1 strain inoculated into the composting raw material could keep the pH level at the range from 7 to 8.5 during composting, which is suitable for the composting microorganisms , and rapid decomposition of the organic materials occurred. Thus, it was confirmed that the NAT strain enables to perform high rate composting by preventing the pH lowering in the early phase of composting for stimulating the proliferation of other thermophiles. Furthermore, it could be found that the cell concentration of the effective bacterium, NA1 strain inoculated into the raw material should be higher than 10^5 colony forming unit/ g dry solid of raw material in order to accelerate the organic matter decomposition in the composting reaction.

20 RELATION BETWEEN MICROBIAL GROWTH, BIOMASS DEGRADATION AND TRACE NUTRIENT AVAILABILITY DURING COMPOSTING. Chervl F. Atkinson **1.** Kim L. Cook[1], Daniel D. Jones[1], [2]Kenneth L. Blackwood and Joseph J. Gauthier[1], [1]Biology Dept., UAB, and [2]PWT Waste Solutions, Inc., Birmingham, AL 35294

During composting of sewage sludge with sawdust as a bulking agent, microorganisms metabolize waste components and produce primarily microbial biomass and carbon dioxide. The rate and extent of composting could become limited if nutrients such as phosphate, ammonia and trace metals are sequestered in the newly formed microbial biomass. Continued composting would then be dependent on the release and turnover of these limiting nutrients. Experiments were conducted to determine the relation between levels of microorganisms, availability of specific nutrients and the potential for degradation of the biomass during composting. Epifluorescence microscopy (DAPI staining) revealed no significant changes in the total numbers of bacterial cells during four weeks of composting. Microbiological assays of the soluble fraction were performed to determine if growth was limited by phosphate, nitrogen, trace elements or organic carbon. Only the soluble organic carbon was limiting. Since high levels of both mesophilic and thermophilic organisms capable of degrading Gram positive and Gram negative cell walls, proteins, lipid and starch could be found throughout the composting period, it is likely that cell turnover is responsible for availability of inorganic nutrients. These data suggest that degradation of insoluble organic compounds (e.g. cellulosic compounds) in the compost mix determines the rate of composting.

Abstract Not Available

22 CHANGES IN BACTERIAL POPULATIONS DURING THE COMPOSTING OF POULTRY UTTER, SAWDUST, YARD WASTE, AND COTTON GIN TRASH. **Larry Softlev. Jr.. Willie McDanieL Debra Tuten, Sheri Grosso, Cindy Kirsch, Richard Strickland, Donald Roush*, Tennessee Valley Authority, National Fertilizer and Environmental Research Center, Muscle Shoals, AL 35660,*University of North Alabama, Florence, AL 35631**

The Tennessee Valley Authority's National Fertilizer and Environmental Research Center (NFERC) has an active program in the use of composting for solid waste management and resource utilization. Emphasis is currently on poultry litter composting to produce materials for value-added processing into potting mixes, soil amendments, and as a component of enhanced organic fertilizers. Additional feedstocks being evaluated include yard waste, sawdust, and cotton gin trash. This paper describes changes in bacterial populations and species diversity over time in windrows managed to optimize aeration, moisture, and carbon to nitrogen ratio during composting. Biweekly samples of poultry litter/sawdust mixtures, yard waste, and cotton gin trash were evaluated to determine total bacterial counts and species identification by fatty acid and Biolog analyses. Pathogenic organisms were also examined using other serological methods. This poster describes changes in microbial population during the composting process as influenced by compost maturity and chemical/physical characteristics.

23 MODIFICATION OF PHYSICAL AND BIOLOGICAL PROPERTIES OF SOIL BY ADDITION OF HOUSEHOLD WASTE COMPOST. **Claire Serra-Wittling*. Sabine Houot and Enrique Barriuso, Laboratoire des Sols, I.N.R.A., Centre de Grignon, 78850 Thiverval-Grignon, France; * Procter & Gamble France, 96 Avenue Charles de Gaulle, B.P. 107,92201 Neuilly sur Seine Cedex, France.**

Solid household waste composting not only represents an interesting alternative of waste disposal, but also provides an organic amendment that can modify soil properties. In this work, a compost originating from separately collected organic household wastes, so called biogenic waste compost, was added to a loamy soil at different application rates. The modifications, after compost addition, of soil physical and biological properties influencing crop production were studied. (1) Soil hydric characteristics, including wetting and retention properties, after compost addition to soil were monitored. (2) Enzyme activities were assayed in soil immediately after compost addition, as well as during a 6-months incubation of soil-compost mixtures. They provided information about the modification of global microbiological activity and specific nutrient cycles in the amended soil. (3) Resistance of amended soil to plant diseases was tested in pot experiments under controlled environmental conditions. The soil was conducive to disease in the different host plant - pathogen systems studied, but addition of compost considerably reduced the incidence of diseases.

45 EFFECTS OF THE USE OF RECYCLED COMPOST AS BULKING AGENT ON THE MICROBIAL FLORA OF A COMPOSTING PROCESS. Kim L. Cook[1], Cheryl F. Atkinson[1], Daniel D. Jones[1], [2]Kenneth L. Blackwood and Joseph J. Gauthier[1]. [1]Biology Dept., UAB, and [2]PWT Waste Solutions, Inc., Birmingham, AL 35294

During composting, microorganisms utilize the waste components of the composting mix as a source of carbon and energy for growth. The physical and nutritional conditions of the compost environment select for organisms able to carry out the composting process. Depending on the survival of various populations (e.g. mesophiles and thermophiles), material which has already been composted may be a potential source of inoculum to enhance the rate of composting. Bench-scale reactors have been designed to simulate the composting environment and experiments carried out which show survival of high levels of both mesophiles and thermophiles during composting. Both mesophiles and thermophiles remained viable during storage of the compost mix for three months. Some species of mesophiles and thermophiles appear to be metabolically inactive outside their temperature range whereas others are able to metabolize even at temperatures that do not support growth. When composted material (recycle) was compared with wood shavings as a bulking agent, there was a sight increase in the rate and extent of composting.

25 **Feasibility of Bioremediating Pestiride/PCB/PAH- Contaminated Soils by Composting.** **H, Kndio Dzantor. Tennessee Valley Authority, P. O. Box 1010, CEB 1C, Muscle Shoals, AL 35660**

Disposal of waste-contaminated soils is emerging as a major and widespread environmental problem. The traditional methods for disposing of waste-contaminated soils, namely excavation and subsequent landTilling or incineration are quite expensive, but these methods do no always address the problem of waste detoxification. Composting of contaminated soil is being investigated as an alternative to traditional methods for waste soil cleanup. Bench scale tests are being initiated in aerated vessels using soil containing aged (>5 yr) mixture of the herbicides alachlor, metolachlor, atrazine, and trifluralin, or soil containing weathered PCBs or PAHs. Data will be presented on the microbial population dynamics and the dissipation of the organic contaminants during the composting process.

26 **THE MICROBIOLOGY OF ENVIRONMENTALLY CONTROLLED COMPOSTING OF SEPARATED GREASE TRAP AND FOOD RELATED SLUDGE WASTE MATERIALS** **Russell S. Joshua. Barry J. Macauley and Craig R. Hudson, Department of Microbiology, La Trobe University, Bundoora 3083, Victoria Australia**

A study was undertaken by La Trobe University and two resource recovery companies to investigate die chemical, microbiological and physical characteristics of rapid environmentally controlled composting of grease trap sludges and food related materials utilizing aerobic and thermophilic conditions. The largely mesophilic population dominated by bacteria and fungi which was present in the initial mix was replaced by a largely thermophilic population dominated by bacteria and actinomycetes at the completion of composting. Total microbial population counts were calculated at 1.1x10^ viable propagules per gram of dry weight compost in the initial mix increasing to 5.4x10 viable propagules per gram of dry weight compost at the completion of composting. The initial grease trap sludges and compost mixes contained a large population of mainly human epidermal and enteric pathogens. Following a 24 hour pasteurization of the compost all pathogenic bacteria investigated had fallen to below detectable levels. The microbial population of the compost was considered to be diverse. A total of 68 species of bacteria were isolated and identified belonging predominantly to the genera *Bacillus* and *Pseudomonas.* The fungal population comprised a total of 47 isolates which were dominated by the genus *Penicillium.* The actfnomycete population was less diverse than the bacterial and fungal populations, a total of 9 actinomycetes being isolated from the compost during processing. The actinomycete population was dominated by species of the *Themoactinospora m&Nocardia.***

27 **REMEDIATION OF PESTICIDE-CONTAMINATED SOIL WITH COMPOST.** **Michael A. Cole. Xianzhang Liu and Liu Zhang, Dept. of Agronomy, Univ. of Illinois, 1102 South Goodwin, Urbana, IL 61801. 217-244-5154.**

Pesticide-contaminated soil from an agrichemical retail site was mixed with either uncontaminated soil or yard waste compost and incubated in a greenhouse. Mixtures were also planted with sweet corn *(Zea mays,* cv. 'Golden Beauty'). Plant growth, bacterial and fungal populations, and microbial activity (as determined by dehydrogenase assay) were significantly greater in compost-containing mixes when compared to mixtures of contaminated and uncontaminated soil at 42 days after planting. Metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-l-methylethyl)acetamide) was degraded in most mixtures with few significant differences among treatments. Trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine) degradation was more rapid in mixes containing compost when compared to 100% contaminated soil or mixes with uncontaminated soil. Degradation of pendimethalin (N-l-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine) was significantly less in unplanted, compost-amended blends in comparison to planted treatments at one site . At a second site, compost + planting also stimulated degradation. Overall, the best results were obtained with a combination of compost addition and planting. The data demonstrate that addition of compost enhances establishment of plants and microbes in soils of poor physical structure and which had been subjected to long-term pesticide contamination and that the pesticides can be degraded if the contaminated soil is treated appropriately. The results suggest that relatively rapid on-site remediation of pesticide-contaminated soil is possible.

28 ENZYMATIC INCORPORATION OF PENTACHLOROPHENOL INTO HUMIC SUBSTANCES FROM SOIL. **Carmen Ruttimann-Johnson and Richard T. Lamar, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin, 53705.**

When pentachlorophenol (PCP) contaminated soil is inoculated with the white rot fungus *Phanerochaete sordida* a dramatic decrease in extractable PCP occurs (around 90% in 6.5 weeks). Only a small portion of it is converted into C02 and volatiles, most of it being converted into soil bound transformation products. It is known that extracellular enzymes produced by microorganisms from the soil can facilitate the covalent binding between xenobiotics and humic substances, a process that eliminates the bioavailability and thus toxicity of the xenobiotic. The present study was undertaken to determine if PCP undergoes binding to humic substances from the soil by the action of enzymes secreted by *P. sordida.* Fulvic and humic acid were extracted from Marshan soil contaminated with ^{14}C-PCP that had been inoculated with *P. sordida* and incubated for 60 days. It was determined that radioactive label from the PCP had been incorporated into the fulvic and humic acids. To study the nature of the binding between PCP and the humic substances similar experiments were done using ^{13}C-PCP, and the humic and fulvic acid obtained were analyzed by ^{13}C-NMR. An *in vitro* approach was used to determine which enzymes produced by *P. sordida* were involved in the binding reaction. First, it was determined that *P . sordida* produces manganese peroxidase and laccase activities when grown on solid substrates. Both enzymes were partially purified and used in separate reactions. The reaction mixtures contained fulvic acid purified from Marshan soil, ^{14}C-PCP, and the enzyme in conditions (pH and cofactors) determined to be the best for each enzyme. In other reactions, low molecular weight precursors of humic material (lignin-derived aromatic compounds) were used instead of the fulvic acid, to see if the fungal enzymes could polymerize them with the PCP. Results on the nature of the binding and the role of the enzymes will be presented.

29 THE FEASIBILITY OF COMPOSTING WASTES CONTAMINATED WITH HIGH VOLATILE PAH **Ana E. Silveiraand Rui B. Ganho. Department of Environmental Sciences and Engineering, New University of Lisbon, Quinta da Torre, 2825 Monte de Caparica, Portugal.**

Recent data show composting as an alternative for treatment of PAH contaminated wastes. Nevertheless the presence of high volatile compounds, like naphthalene, might compromise the interest of this treatment alternative and thus its careful evaluation is justified. A bench scale composting system was built to evaluate, through a material balance, the effect of inoculation, concentration, temperature and aeration rate on the naphthalene biodegradation/volatilization ratio. The composting experiments have been performed at constant temperature with on-line C02, air flow and temperature measurements. Naphthalene concentration is measured in solid, aquose and gas phases by HPLC and GC. The Steam Destination Extraction (SDE) has been used to isolate naphthalene from the solid matrix. Naphthalene has been monitored continuously in the air outlet using Poropak Q traps. Preliminary results show that 77% of naphthalene was lost after 3 days of composting a sinthetic substrate through a nonacclimated population at 40°C and 64% of initial moisture. A seed from a wastewater activated sludge treatment facility has been acclimated at 40°C to the sinthetic substrate contaminated with naphthalene. Results with the seed and higher concentrations of naphthalene will be also presented.

3° ENVIRONMENTALLY SAFE ON-FARM COMPOSTING.
Christopher S. Lufkin and Ted Loudon.
Department of Agriculture Engineering, Michigan State University, East Lansing, Michigan 48824-1323.

This presentation will summarize aspects of a project to study and demonstrate the use of on-farm windrow composting for adding value to manure and yard waste. Improved methods of manure management are being sought which will control odors and render the material more easily transported. Farmers need to move manure further from large livestock facilities or sell it as a product. Municipalities are facing the need to develop new methods of disposing of municipal yard wastes.

The study incorporates the use of a geosynthetic fabric designed to shed water off of compost windrows while allowing gaxeous exchange. Drainage lysimeters re used to monitor leaching in a very sandy soil condition. The geosynthetic faerie cover apperas to be very effective in minimizing water movement through windrows.

The paper will report on daily C02 production, oxygen consumption, temperature variation, compost quality, the collection of leachate, year and compost production, labor and machiner requirements, and an overall evaluation of the practicality of composting on livestock farms.

31 EFFECT OF STRAW COMPOSTING ON THE DEGRADATION AND STABILIZATION OF CHLOROPHENOLS IN SOIL. **Pierre Benoit and Enrique Barriuso, Laboratoire des Sols, I.N.R.A., Centre de Grignon, 78850 Thiverval-Grignon, France.**

Wheat straws are currently used as crop residues to enhance soil stability and biological activity of cultivated soils. Non composted and composted wheat straw have been compared regards to their stabilization properties towards 2,4-dichlorophenol and 4-chlororophenol. Such molecules are potentially present in soils as they are formed through the aerobic degradation of phenoxyherbicides and others chlorinated pesticides. Using l^C ring labelled molecules, the transformations of these compounds have been followed during soil incubation experiments after their retention on composted and non composted straw. Straw composting changes the chemical and physical properties of the original material and modifies some biological activity characteristics like the size of bacterial and fungal populations and the oxidative enzymatic activities. For both pollutants, straw composting decreases their mineralization and parallely increases the formation of non-extractable or bound residues. This seems to be directly related to the activity of the microflora grown during the composting of straw.

32 THE EFFECTS OF LIGNOCELLULOSE STRUCTURE AND COMPOSITION ON THE DEGRADATION AND MINERALIZATION OF ATRAZINE. **Nishant Rao, and Hans E. Grethlein, Dept. of Chemical Engineering, Michigan State University, E. Lansing, MI 48824.**

Organisms capable of degrading lignocellulosics have been shown to degrade a variety of pesticides due to their non-specific lignin oxidizing systems. The ability of compost microorganisms to gratuitously metabolize pesticides offers a relatively inexpensive and environmentally safe method of pesticide disposal. In this study we studied the fate of atrazine in composting environments with lignocellulosics as the growth substrate. Four substrates (untreated poplar wood, steam exploded poplar wood, ammonia exploded poplar wood, and shredded newspaper) were selected based on their differing compositions and pore size distributions. These substrates were composted in 2 l lab-scale composters with 500 ppm of atrazine loaded onto each. The inoculum was obtained from finished wood compost. ^C-ring-UL atrazine was added to replicate composters to determine the rate and extent of atrazine mineralization. Atrazine degradation was monitored by extraction and GC analysis of the degradation products. Rates of degradation of substrate components (lignin, cellulose, and hemicellulose) were measured using the quantitative saccharification technique and were correlated with the rate of atrazine degradation. Results showed that the ammonia exploded poplar wood had the highest rate and extent of composting of the biomass among the substrates chosen. However, mineralization of atrazine seemed independent of the substrates composting rate.

33 FATE OF THE LAWN CARE PESTICIDES 2,4-D AND DIAZINON DURING YARD WASTE COMPOSTING. **Frederick C. Michel Jr., C. Adinarayana Reddy, Larry J. Forney,** ***Department of Microbiology and NSF Center for Microbial Ecology, Michigan State University, East Lansing MI 48824-1101***

One of the primary concerns with yard waste compost production and use is the fate of lawn care pesticides. In this study, [U-ring-^{14}C] 2,4-D (16 ppm) and Diazinon (11 ppm) were applied to a grass and leaf mixture (1:2) and composted under simulated composting conditions (60% moisture, 60 C) in a laboratory scale system. The fates of the pesticides were determined by measuring the amounts of the volatilized from the compost and mineralized to ^{14}C02, and by fractionating the ^{14}C remaining in the compost into organic soluble, water soluble, Na2P407 soluble, and insoluble (humin) fractions. The Na2?407 soluble fractions were further fractionated into fulvic acid, humic acid, and non-humic fractions and applied to a gel permeation chromatography column to determine the estimated molecular weights of the extractable metabolites. Results showed that at the end of a composting period of 50 days in which 46% of the total organic matter was mineralized, 47% of the 2,4-D and 11% of the added Diazinon was mineralized and negligible amounts were volatilized. The majority of the *^{14}C remaining in the compost after 50 days of romposting, was present in the water soluble (Diazinon) or humic acid (2,4-D) fractions and the humin (non-extractable) fraction. The estimated molecular weights of the pesticide residues in the Na2P407 extracts were greater than the parent compounds.

34 **BIODEGRADABLE PLASTICS IN COMPOSTING.** **Ludwig Streff. Werner Bidlingmaier, Universitat GH Essen, FB 10, Abfallwirtschaft, UniversitatsstraBe 15, D-45141 Essen, Germany.**

In waste-management it will be important in the near future to close lifecycles of material. To be mentioned are: 1) completed industrial cycles of material through recycling-measures; 2) completed cycles of material in the biosphere. Terms like regrowing raw-materials, biodegradable materials and composting are to be considered. For biodegradable plastics - these products are increasingly pushing on the market - it is necessary to construct guidelines which control if and when such waste can be supplied to a composting plant, because "biodegradable" doesn't mean that these products can be degradated in a real running plant. That's the reason why it is important to define the following Terms and to develop test-methods: 1) biodegradable; 2) compostable in principle; 3) compostable in realistic periods of time; 4) disturbing material For the composting or not. When these Terms have been cleared in detail, it is possible to make statements For suitibilify of waste in biological utilization. For determination of compostability (in principle and in technical plants) methods have been developed based on respiration activity analysis in 5 1 vessels and determination of degradation in defined volumina in real running plants. The degradation has been determined gravimetrically and by analysis of the carbon content. The results showed pregnant differences in the velocity of degradation For various biodegradable plastics. Laboratory- and field-methods showed comparible results.These are the bases which enables us to prove the compostability beside the general biodegradability by special determinations of degradation.

35

Abstract Not Available

36 **CPMAS ^{13}C-NMR SPECTROSCOPY AS A PREDICTIVE TOOL FOR COMPOST STABILITY AND SOIL HEALTH.** **Harry J. HoitInk[1]. Larry V. Madden[1], and Ed G. Wilson[2], department of Plant Pathology, Ohio Agricultural Research and Development Center, The Ohio State University, Wooster, OH 44691. Department of Chemistry, University of Akron, Akron, OH 44325.**

CPMAS ^{13}C-NMR spectroscopy was utilized to monitor biological energy availability in soil organic matter and how that affects microbial species composition and the potential for plant disease suppression. The disappearance of bioavailable energy in composts, peat, etc. was monitored directly with CPMAS-^{13}C-NMR spectroscopy (NMR). As NMR detectable energy declined, the rate of hydrolysis of fluorescein diacetate decreased and suppressiveness to *Pythium uHimum*, a soilborne plant pathogen, was lost and disease developed. During this decline in soil health, the composition of bacterial taxa in the soil and rhizosphere changed even though species diversity, based on richness and evenness was not affected significantly. Furthermore, microbial biomass and activity based on uptake of ^{14}C acetate into microbial biomass did not decline. Finally, populations of microorganisms that can induce biological control of the disease were replaced by those that can not. In conclusion, NMR could be developed to predict compost stability and soil health in terms of the potential for biological control of soilborne plant pathogens.

37 **MECHANISM OF ADSORPTION ON ALUMINA OF A COMPOST LEACHATE DOC BY SOLID STATE ^{13}C NMR.** **Robert L. Wershaw.[2]EIma C. Llaguno and [1]Jerry A. Leenheer, [1]U.S. Geological Survey, Arvada, CO, 80002 and [2]Institute of Chemistry, University of the Philippines, Diliman, Quezon City, Philippines, 1101**

The formation of humus coatings on mineral surfaces was investigated using dissolved organic acids from a leaf litter compost leachate and alumina as a model system. The alumina adsorption studies were undertaken with the unfractionated DOCand its hydrophobic and hydrophiUc fractions at the natural leachate pH of 7 and at three ionic strengths (0 M NaCI, 0.01 M NaCl and 0.1O M NaCl). The change in pH and the organic carbon adsorption density were measured while the structure of the organic material adsorbed on the alumina was characterized by ^{13}C NMR using cross polarization-magic angle spinning (CP-MAS) techniques. The solution pH was observed to increase upon adsorption of the DOC's on alumina. At constant initial DOC concentration, adsorption increased with salt concentration but resulted in lower pH increments. The solid state *^C NMR spectra provided evidence for initial adsorption of bicarbonate ion on the alumina surface and subsequent displacement of the ion upon adsorption of the organic acids. The effect of adsorption on the various structural components of the humus polymers will be discussed.

38 FLUORESCENCE SPECTRAL AND LIFETIME STUDIES OF COMPOST LEACHATES. **Sherry L. Hemmingsen. Linda B. McGown, Duke University, P. M. Gross Chemical Laboratory, P. O. Box 90348, Durham, North Carolina 27708-0348.**

As concerns continue to rise over how to dispose of accumulating solid organic wastes (grass clippings, leaf litter, animal manure, etc.), alternative waste management practices have become increasingly popular, especially in the area of composting methods. Composted wastes can be agricmturally recycled through application as an organic amendment to soil. However, compost maturity plays an important role in their successful use in agriculture. Many spectroscopic procedures are being developed to characterize composts, as well as to define a maturity index for them. Our group has used total lurriinescence spectral and lifetime techniques to study human sera, coal liquids, and humic substances. Recendy, we have begun to investigate a compost leachate extracted from a municipal composting site which primarily receives its plant material from oak leaf litter. In this talk, we will discuss the fluorescence characterization of this compost leachate. Total luminescence spectra reveal only a single, broad fluorescence emission peak which shifts to shorter wavelengths as concentration of the leachate decreases. Analysis of lifetime data collected at several emission wavelengths produces a multi-component fit spanning approximately 0.5 to 10 ns which is similar to results from previous work on commercial humic acids.

39 APPLICATION OF SPECTROSCOPIC ANALYSIS TO THE COMPOSTING PROCESS IN A BENCH SCALE COMPOSTING SYSTEM. David Y. Tseng. Sam Traina, and Jeffrey J. Chalmers. Dept. of Chem. Eng., Dept. of Agronomy. Ohio State University. 140 W. 19th Ave. Columbus, OH 43210

In recent years, composting has become an effective method to solve many solid waste problems. However, a lack of fundamental understanding of the process has resulted in inadequate process control, odor formation, pathogen formation, etc. In order to achieve a fundamental understanding of the composting process, a lab-scale system has been developed. In this system the composting process is controlled, by way of a computer, to maintain a constant temperature, oxygen and moisture content. With this system, the effect of different environments, determined by the researcher-not the process, can be studied with respect to the rate and type of degradation, the type of organisms present, the oxygen demands, etc.

In addition, a unique method using FT-IR has been developed to determine the amount and type of degradation of organic compounds. Through the use of appropriate internal standards it is possible to quantify the type and amount of different organic compounds during a particular experiment. This technique, combined with the system outlined above, it is possible to more accurately study the composting process than previously possible.

40 ANALYSIS OF COMPOSTS BY CONVENTIONAL AND ***in situ*** METHYLATION PYROLYSIS. C. Saiz-Jimenez, J. Cegarra[1], A. Roig[1], B. Hermosin, J.J. Ortega-Calvo, C. Paredes[1] and M.P. Bernal[1], Instituto de Recursos Naturalesy Agrobiologia, C.S.I.C, Apartado 1052, 41080 Sevilla and [1]Centro de Edafologia y Biologia Aplicada del Segura, C.S.I.C, Murcia, Spain

Mixtures of olive mill waste water, cotton waste, corn straw, sewage sludge and poultry manure were composted during two months using the Rutgers system and allowed to mature for two additional months. Conventional pyrolysis of fresh and composted materials indicated that composting process alters the composition of parent materials. The application of a recently introduced method, simultaneous methylation-pyrolysis, provides a more representative picture as polar carboxyl- and hydroxyl-containing compounds are evidenced in the chromatograms due to protection of functional groups. Conventional ***vs*** methylation pyrolysis data and the significance of evaporation/pyrolysis products regarding structural implications are discussed.

41 ANALYSIS OF INORGANICS AND SEMI-VOLATILE ORGANICS IN COMPOSTED WASTE MATERIALS.

David E. Stilwell Brian D. Eitzer, and Craig L. Musante, Connecticut Agricultural Experiment Station, Box 1106, New-Haven, CT 06504.

The use of composted municipal solid waste (MSW) on agricultural soils offers an attractive alternative to landfill or incineration. However, prior to widespread use, the amounts of toxic compounds in the compost need must be identified and quantified. We wffl present our results on the determination of inorganic constituents (including heavy metals) and semi-volatile organic pollutants (including PAH's) in MSW compost. The compost was made from compostable waste collected at a public event (Norwalk Oyster Festival). The semi-volatile organic pollutants in the compost were detenrrined using mass spectrometry with an ion trap detector. Samples for inorganic analysis were obtained following a dual stage design, allowing for determination of batch homogeneity. The samples were digested in a microwave and the analytes were detennined using atomic spectroscopy. The inorganic constituents, spike recoveries, and compost homogeneity will be compared with our data from MSW compost made from rnixed waste and from source-separated waste.

42 BIOAVAILABILITY OF HEAVY METALS FROM COMPOST.

P.R. Warman, Nova Scotia Agricultural College, P.O. Box 550, Truro, Nova Scotia, Canada. B2N 5E3.

A committee has been struck to establish appropriate compost standards for Canada. Five aspects of compost safety and quality are being evaluated; probably the most controversial issue is the standards for metals in compost. Instead of basing the potential use of compost on the total content of applied metal, proposed regulations should adhere to the No Observed Adverse Effect Level (NOAEL). To this end, we have been conducting research on the bioavailability of 11 metals to Swiss chard, a known metal accumulator. Plants have been grown in compost-amended soils in a growth room using five compost to soil ratios (0 to 100% compost). Different soils and composts have been used. Two experiments used a sewa'ge sludge-racetrack manure compost while three experiments used a racetrack manure-grass clippings compost supplemented with 'soups' of the 11 heavy metals. Metals in soils (total and 'plant available') and plant tissue have been correlated and total metal uptake of the 11 elements by the chard has been evaluated. The presentation will highlight the most important results of the experiments.

Abstract Not Available

Abstract Not Available

,6 HOT ELECTRON DETECTION IN PHOTOELECTROCHEMICAL CELLS WITH GaAs/AlGaAs SUPERLATTICE/ELECTROLYTE JUNCTIONS. **David K. Watts. Carl A. Koval. Department of Chemistry and Biochemistry, Campus Box 215, University of Colorado, Boulder, CO 80309.**

In any photoconversion device, matching the solar spectrum to the absorption spectrum of the photoconversion device can present severe constraints on the efficiency of solar energy conversion. Small bandgap semiconductors can be used in photoelectrochemical cells in order to collect a large fraction of the solar spectrum. However the conversion of higher energy photons is highly inefficient. The energy of an excited electron in excess of the bandgap is wasted due to rapid thermalization. When electrons above the edge of the conduction band, or "hot" electrons thermalize, the excess energy is wasted. Superlattices prepared at NREL by MOCVD consist of alternating thin layers of GaAs and $Al_xGa_{1-x}As$ grown onto a highly doped p-GaAs substrate. The A^Ga^As layers act as barriers to the electrons while the GaAs layers form wells in which the energy levels are quantized. Excitation to the different energy levels produces different energies of photogenerated hot electrons that can be ejected into solution. Various systems were examined for the detection of hot electrons using rotating platinum ring-semiconductor disk electrodes.

47 MEASUREMENT OF ELECTROSTATIC CHARACTERISTICS AT SOLID/LiqUID INTERFACES, John. M. Pope and Daniel A. Buttry, University of Wyoming, Laramie, Wyoming 82071-3838.

By observing the Stark effect fox chromophories in electric fields near metal surfaces, we have developed a new method of spectroscopic measurement of intexfacial electric fields and other electrostatic characteristics at solid/liquid interfaces. We have monitored the peak fluorescence of chromophores, immobilized on metal surfaces using self-assembly techniques, as experimental conditions including surface potential and electrolyte concentration were varied. This method allows quantitative calculations of the electric field at the chromophore to be made. The -magnitude and behavior of the electric fields investigated suggest several interesting applications. The monolayers were characterized by RAFTIR,spectroscopy.

48 DETERMINATION OF LARGE HETEROGENOUS RATE CONSTANTS USING NANOELECTRODE ENSEMBLES. **Vinod P. Menon and Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins, CO 80523**

An electroless deposition method has been developed for the fabrication of nanoelectrode ensembles using commercially available polycarbonate membrane filters as templates. Ensembles with individual electrode radii as small as 50A have been fabricated.These ensembles act as partially blocked electrodes and have a very low fractional electrode area. Due to the apparent slowing down of rate constants at partially blocked electrodes, these ensembles can been used to determine heterogenous rate constants for extremely fast redox couples. Rate constants as high as 70cm/s have been obtained for a derivatlzed ferrocene couple. Furthermore these ensembles show detection limits three orders of magnitude lower than conventional macrosized electrodes. Some of these kinetic and detection limit data will be presented.

a "THROUGH SPACE" vs. "THROUGH BOND" INTERACTIONS IN RIGIDLY LINKED HOMODINUCLEAR COMPLEXES. Daniel Derr, Suzanne Ferrere, and C. Michael Elliott, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

The metal-metal interactions in a series of rigid homodinuclear iron complexes will be discussed. Each contains two iron(II) atoms connected by three bis-bipyridyl alkane (or related) ligands. The complexes have been prepared utilizing bridging moities of the type -CH2-X-CH2- where X is nothing, methylene, or a heteroatom. Characterization of these complexes indicates nearly identical iron-iron distances. The structural rigidity of the complexes due to the triple bridge presumably is what causes this. Additionaly, the bond connectivity is isolated as the only variable between the different complexes. Preliminary results indicate a "through-space" rather than a "through-bond" mechanism for the interaction between the metal centers of each complex.

50 MOLECULAR RECTIFICATION OF CURRENT IN SELF-ASSEMBLED REDOX BILAYERS. Jody Redepenning. Jacqueline M. Flood, Efrain Castro-Narro, Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304

Murray and co-workers have demonstrated a thermodynamic/kinetic scheme that can be used to produce cunent rectification and charge trapping at electrodes modified with thin polymer films. This was accomplished by coating electrodes with two layers of electroactive polymers, each of which had a different formal potential. In this seminar we describe our efforts to achieve cunent rectification in self-assembled layers on electrode surfaces. The self-assembled layers are constructed from molecules in which two redox couples are tethered together with an aliphatic chain. These redox sites are tethered to the surface by an alkanethiol group. After reviewing the fundamentals of current rectification in redox bilayers, we will describe the propensity of our self-assembled films to act as molecular diodes.

51 INDIVIDUAL MICROELECTRODE BEHAVIOR AT LOW DENSITY ARRAYS OF MICROELECTRODES. C. Anthony Pitrat and Charles R. Martin, Colorado State University, Fort Collins. Colorado 80523.

Microelectrode behavior has been shown to be useful for a variety of applications. One of the major drawbacks of microelectrode behavior, however, is that the currents at small microelectrodes are very small. We have developed low density arrays of microelectrodes that show the behavior of individual microelectrodes while giving currents that can be easily measured. Low density arrays are arrays where the elements are spaced far enough apart that during the time scale of the experiment they remain independent. Experimental behavior of these arrays is shown to be consistent with individual microelectrode behavior.

52 INVESTIGATIONS INTO THE $La_2Cu04+3$ AND RELATED SYSTEMS: SYNTHESIS, THIN FILM PREPARATION AND ELECTROCHEMICAL OXIDATION, William. J. Donahue, and Bruce. A. Parkinson, Department of Chemistry, Colorado State University, Fort Collins Colorado, **80523** and Robert. L. Harlow, Micheal. K. Crawford, and Eugene. M. McCarron, DuPont Central Research, Wilmington, DE **19898.**

The oxidation level (d) of La2Cu04+a has been recognized as the primary factor determining superconductivity and the transition temperature in these and related materials. We have electrochemically oxidized La2Gu04 and $La2-_xNd_xCu04$ to investigate their phase behavior at different oxidation levels and Nd contents. We have also developed a simple low temperature method to prepare thin films of these materials. We have characterized the films using SEM, AFM, and X-ray diffraction. Kinetics of the electrochemical oxidation of the films and bulk materials will be presented.

53 TEMPLATE SYNTHESIS OF METAL NANOPARTICLES AND OPTICAL ORIENTATION EFFECTS, **Deborah L. KunkeL Vinod Menon, and Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins, CO 80523**

Electroless deposition of gold or silver into microporous polycarbonate membranes has been used as a template method of synthesis to obtain metal particles of a known diameter, length and orientation. By using membranes with pores in the 100 A diameter range, we can synthesize metal nanoparticles that are much smaller than the wavelength of light in the visible region of the spectrum. We can thus simulate the optical properties of the metal/polycarbonate composites using effective medium theory. The optical properties of the composite films depend upon the optical characteristics of the individual components as well as the size, shape and orientation of the particles in the incident field of the light. We compare the size and shape effects for gold/polycarbonate films to those previously presented for gold/alumina composites. In addition, we also discuss the effects of changing the orientation of the metal particles in the incident field of the light and compare the experimental results to spectra simulated via a modified Maxwell-Garnett effective medium model.

55 OPTICAL PROPERTIES AND CHARACTERIZATION OF ALUMINUM NANOMETAL/POROUS ALUMINUM OXIDE COMPOSITE THIN FILMS: TRANSPARENCY THROUGHOUT THE VISIBLE REGION OF THE SPECTRUM. **Gabor L. Hornvak. K.L.N. Phani, Benjamin P. Berggren, and Charles R. Martin, Colorado State University, Department of Chemistry, Fort Collins, Colorado 80523.**

Computer simulated spectra of a Maxwell-Garnett effective medium theory treatment of aluminum nanometaValiiminurn oxide composite thin films show transparency throughout the visible range of the spectrum. According to our simulations, aluminum nanoparticles existing within the quasistatic infinite wavelength limit possess plasmon resonance absorption below 200 nm. We present an experimental strategy for electroplating metallic aluminum into porous aluminum oxide host templates by means of a toluene/ aluminum bromide/potassium bromide/trimethylchlorosilane system. For particles with larger dimensions, where scattering cannot be neglected, our dynamical Maxwell-Garnett effective medium treatment is employed to explain the composite spectra.

56 **ELECTROCHEMISTRY OF METHANOL AT LOW INDEX CRYSTAL PLANES OF PLATINUM: AN INTEGRATED VOLTAMMETRIC AND CHRONOAMPEROMETRIC STUDY.** **Enrique Herrero[3], Krzvsztof Franaszczukb. and Andrzej Wieckowski[n], ^Department of Chemistry. University'of Alicante, Spain, ^Department of Chemistry, University of Illinois, 600 South Mathews Avenue, Urbana, Illinois 61801.**

We have studied a catalytic decomposition of methanol on low Miller index platinum surfaces, Pt(lll). Pt(llO) and Pt(lOO) in perchloric, sulfuric and phosphoric acids at room temperature. The instantaneous methanol oxidation current is unaffected by the methanolic CO formation (surface poisoning) and depends on platinum surface structure, and composition of supporting electrolyte with respect to the anions. The highest oxidation current. 156 mA-cm"^, is observed with the Pt(llO) electrode in perchloric acid solution at 0.200 V vs. Ag/AgCl reference. In terms of turnover, this current translates to 163 molecules-(Pt site)"'^"'. a high rate exceeding previous expectations in methanol electrode kinetics. Overall, the oxidation *current* changes by three orders of magnitude between the extreme cases examined in this study. Breaking up the total effect into individual components shows that the *surface* geometry and anionic effects are roughly comparable. Therefore, we have an evidence that anion-platinum interactions are as important in determining the methanol oxidation rate, as is the surface geometry of the Pt catalyst. Being encouraged by the magnitude of the oxidation current, especially with the Pt(llO) electrode, and by the control of the oxidation process through the structural and electrochemical variables of this research, we also report that the rate of methanolic CO formation follows the same pattern as does the oxidation current. Namely, the CO poisoning is the highest for the Pt(llO) electrode in perchloric acid and the slowest with the Pt(lll) electrode in phosphoric acid. We conclude that optimizing the structure of clean platinum, and solution composition, is not a sufficient remedy for platinum deactivation, and that the CO poisoning process must be addressed with new force in basic research on platinum fuel cell catalysis.

57 **SURFACE ELECTROCHEMISTRY OF DIYDROXYQUINOLINES: COMPARISON OF PENDENT AND NON-PENDENT 5,8-DIHYDROXYQUINOLINE.** **Donald C. Zapien. Trang Y. Vo and Angelique D.Willard, Department of Chemistry, Campus Box 194, University of Colorado at Denver, P. O. Box 173364, Denver, Colorado 80217-3364**

Quinolinequinones have been the subject of some studies using epr and electrochemistry, particularly in their reduced, dihydroxy form. Quinolinequinone is the central portion of the skeleton of some biologically important compounds. However, most of the electrochemical studies on these compounds have examined the redox properties of the dissolved species only. This work investigates some of the surface electrochemistry of 5,8-dihydroxyquinolines. Because of its similarity in structure to naphthalene, it is of interest to compare the surface electrochemical properties of analogous naphthalene and quinoline derivatives. Two types of quinoline derivatives have been synthesized, 5,8-dihydroxyquinoline (I) and 5,8-dihydroxy-7-(3'-methylthio)propylquinoline (II). Adsorbed layers of (I) are formed by immersing an electrode into a solutions containing the adsorbate at controlled potential. The cyclic voltammetry of the adsorbed layer is then compared to that of adsorbed 1,4-naphthohydroquinone (III). Compound (II) possesses a three carbon-long appendage at the 7-posiuon. The surface electrochemistry of this derivative will be discussed and compared with that of its naphthalene analog, l,4-dihydroxy-2-(3'-methylthio)propyl-naphthalene (IV).

58 **INVESTIGATIONS OF HIGH QUANTUM YIELD DYE SENSITIZATION PROCESSES ON A TWO-DIMENSIONAL SEMICONDUCTOR.** **Laura I. Sharp. Xiumei Dou and Bruce A. Parkinson, Department of Chemistry, Colorado State University, Fort Collins, CO 80523**

Dye sensitization has the potential to extend the spectral range of large band gap semiconductors. Dye molecules adsorbed on the surface of the semiconductor can absorb visible light to reach an excited state. When the energy levels of an adsorbed dye molecule overlap with the conduction band of the semiconductor, an electron in an excited state of the dye can be injected into the conduction band. Two-dimensional metal dichalcogenide semiconductors such as SnS2 which demonstrate high injection quantum yields are suitable for studying the fundamentals of dye sensitization. In particular, we are interested in understanding the electron transfer mechanism of dye molecules. Enhancement of the quantum efficiency per incident photon by at least one order of magnitude with respect to an unetched surface was obtained via photoelectrochemical etching of a SnS2 photoanode. The results of this study will be presented.

59 **SURFACE CHARACTERIZATION OF IMMOBILIZED AMINES ON CARBON FIBER SURFACE.** **Jimmy C. M. Peng, and Daniel A. Buttry. Department of Chemistry, P.O. BOX 3838, University of Wyoming, Laramie, WY 82071.**

Nucleophilic thermal reaction and electrochemical oxidation of amines allow the covalent bonding of these molecules directly to the electrophilic vinyl groups on the carbon fiber surface. The structure of the bonded layer is studied by voltammetry, X-ray photon spectroscopy (XPS), Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR) and other methods. Mechanisms are proposed which involve nucleophilic attack of amines at the electrophilic vinyl groups on the fibers. An embedded single fiber test is used to measure the interfacial shear strength between fiber and matrix for the didecylamine and 1,6-diamino-hexane reactions. The mechanical testing results and polarized light observations of these two reactions give direct evidence for the nucleophilic reaction of amine onto carbon fiber.

60 **INVESTIGATION OF CHANGES IN REDOX BEHAVIOR OF CONDUCTING POLYMERS IN THE PRESENCE OF NEUTRAL ORGANICS.** **Susan M. Hendrickson. Daniel L. Feldheim, Michael Krejcik, and C. Michael Elliott, Department of Chemistry, Colorado State University, Fort Collins, CO 80523**

We have discovered that the redox properties of certain conducting polymers undergo drastic changes in the presence of trace amounts of neutral molecules in aqueous solution. Poly(N-methylpyrrole), for example, displays a shift in its redox waves toward more positive potentials when dichloromethane is introduced into aqueous solution while the anodic and cathodic currents generally remain the same. Poly(3,4-diphenylpyxrole), in contrast, is electrochemically inactive in 0.1 M NaC104(aq) solution but undergoes "normal" oxidation and reduction in the presence of trace dichloromethane. Our ultimate goal is to adapt this system for use as an amperometric sensor for contaminants in waste water. To that end, we have studied this system with cyclic voltammetry, spectroelectrochemistry, electrochemical quartz crystal microgravimetry and flow injection analysis. The movement of dopant ions through these films in the presence and absence of trace organics in solution will be discussed.

61 RESPONSE MECHANISM OF POTENTIOMETRIC HEPARIN SENSOR: A NEW APPROACH FOR THE DETECTION OF POLYIONIC MACROMOLECULES. **Bin Fu: and Mark E. Meyerhoff Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109-1055.**

To date, the use of classical polymer membrane-based potentiometric sensors has been limited to the analysis of small ions (e.g., K^+, Na^+, Ca^{2+}, etc.) due to the sensitivity limitations imposed by the Nernst equation for multiply charged polyions. However, it has recently been shown *[Anal. Chem.* 1993, *65,* 2078] that a specially formulated plasticized PVC membrane exhibits significant response toward polyanioic heparin, frequently used in medicine as an anticoagulant. While true equilibrium polyion response, obtained for low heparin concentrations only after very long equilibration times (>20 h), yields the expected Nernstian response slope of < 1 mV/decade, the observed large and reproducible EMF response to clinically relevant heparin concentrations (~10^{-7} M) is ascribed to a steady-state kinetic process. A quasi-steady state model describing this non-equilibrium response will be presented. With this model, the uniqueness of the polymer membrane composition (e.g., very low plasticizer content, strictly controlled cationic site concentration, etc.) required to achieve analytically useful heparin response will be explained. Other observations which are unusual for typical ion-selective electrodes can also be understood with this model; e.g. cylindrical configuration coated wire electrode exhibits a lower detection limit, stirring of the sample has a profound influence on the sensor potentiometric response, etc.. Practical working conditions and limitations of the sensor will also be discussed.

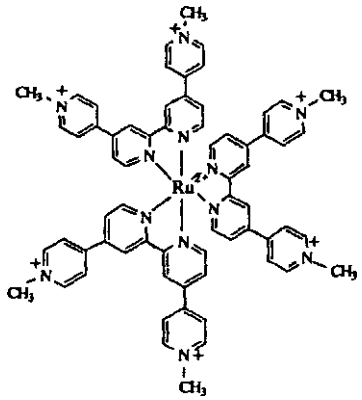
62 Nickel Oxide Amperometry, Convection and Alkaline Earth Effects. **C J. Gartzke and CO. Huber. Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, P.O. Box 413, Milwaukee, WI 53201-0413**

Anodic amperometry at a nickel electrode for representative pollutant organics uses solution stopped flow for mass transport control. Applied potential stepping from -1.0 for 15 seconds to +0.5 v vs SCE is used. The linear analytical range extends to near 1 micromolar for several analytes including carbohydrates, amines and phenol. Calcium enhances the signal, in remarkable contrast to conventional convective amperometry in which calcium is a strong inhibitor. It is proposed that the larger pH gradient in the stopped flow method inhibits formation of calcium-oxygen linkages and also that calcium cations partially block proton exchange sites in the surface lattice.

63 **A STUDY OF A SERIES OF MULTICOLOR ELECTROCHROMIC RUTHENIUM COMPLEXES.** **Francois Pichot. Jeff Beck, David Underwood and C. Michael Elliott, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.**

Ruthenium tris-bipyridine complexes usually possess very rich electrochemistry as well as interesting spectral properties. Of particular interest is the complex tris(5,5' - dicarboxyethyl - 2,2' - bipyridine) ruthenium (II) which displays unique electrochromic properties : To each of its seven oxidation states correspond a specific color of emission. The influence of the bipyridine functionality on the electrochromic properties of this complex has been investigated. The ester substituents on the bipyridine ligands were replaced with other electron-withdrawing groups such as amides, nitriles and ketones. The corresponding ruthenium complexes were prepared and characterized by cyclic voltammetry, bulk electrolysis and spectroelectrochemistry. Their interesting electrochromic behavior will be discussed.

64 **A USEFUL SIX-ELECTRON REDUCING AGENT? SYNTHESIS AND CHARACTERIZATIONS OF METAL COMPLEXES WITH ALKYLATED QUATERPRYIDINE LIGANDS.** **Jody Redepenning, Sangsub Han. Marc A. Larson, Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304**



Ruthenium (II) polypyridine complexes have received a great deal of attention as components of schemes to use photoactiviated electron transfer reactions for solar energy conversion. Many of these compounds exhibit rich electrochemical and photochemical properties. We have recently prepared a number of new complexes using alkylated 2,2':4,4":4',4"'-quaterpyridyl (qpy) ligands. In this seminar we describe the homogeneous electrochemistry of methylated quaterpyridinium complexes such as the one shown to the left. These complexes can be reduced by up to twelve electrons. Up to six (unresolved) pyridinium reductions can be observed over a narrow potential range. As many as six additional one-electron reductions can be resolved at more negative potentials. Syntheses of the ligands and complexes will be provided along with spectroelectrochemical and nmr characterizations.

65 **SEPARATION AND CONCENTRATION OF GASES UTILIZING ELECTROCHEMICALLY MODULATED COMPLEXATION.** **Carl A. Koval. Patricia Terry, Richard D. Noble. Depts. of Chemistry of Chemical Engineering, Univ. of Colorado, Boulder, CO 80309-0215.**

Electrochemically modulated complexation (EMC) is a process that allows solutes to be extracted selectively from one phase and to be concentrated subsequently in a second phase. This type of process has potential application to chemical processing and environmental remediation. The process utilizes redox active molecules (carriers) that bind the solutes in one oxidation state yet show little binding affinity when the oxidation state is changed. Electrochemical cycling of Cu(II)/(I) in aqueous chloride electrolytes allows carbon monoxide to pumped selectively from low (2 psi) to high (20 psi) pressures. Use of flow electrolysis cells and hollow fiber membrane contactors allows this process to be carried out continuously. Factors that influence the rate, maximum pressure difference, and energy efficiency of EMC gas pumping will be discussed.

66 **A COMPARISON OF RURAL AND URBAN ALDEHYDE CONCENTRATIONS.**
Randolph Eisenhardt. CU-Denver, Chemistry Dept., Campus Box 194, P.O. Box 173364, Denver, CO 80217-3364

Low molecular weight aldehydes and acetone are by-products of combustion of C5-C10 fuels (Gasoline). Determination of the ambient concentrations of these by-products allows for interpretation of air quality in the area being tested. The objective of this research project is to determine the concentrations of low molecular weight ketones and aldehydes, at a rural site, (Barr Lake State Recreation Area), and compare them to urban concentrations (downtown Denver). This information is being used to examine the photochemistry occurring in the atmosphere as air migrates out of an urban area to a rural area. A predetermined volume of air to be analyzed is moved through DNPH coated silica cartridges. The aldehydes and ketones retained on the cartridge are then extracted with acetonitrile and analyzed by HPLC. The resulting chromatograms have shown differences in concentrations of aldehydes and ketones between the rural and urban locations. Preliminary results indicate higher levels of acetone and acrolein present at Barr Lake, with levels of aldehydes comparable to those found in Denver.

67 **SUPERCRITICAL CARBON DIOXIDE EXTRACTIONS OF ORGANIC CONTAMINANTS FROM LOW LEVEL MIXED WASTE AT THE ROCKY FLATS PLANT, COLORADO.**
Paul Buckley, Robert Sievers, Barbara Watkins. Cooperative Institute for Research in Environmental Sciences (ORES), Campus Box 216, University of Colorado, Boulder, Colorado, 80309-0216

Over thirty years of nuclear weapons production at the Rocky Flats Plant (RFP) northwest of Denver has resulted in the accumulation of significant quantities of industrial refuse (rags, cloth, glass, metal, etc.) contaminated with both low level transuranic elements and with varying levels of organic solvents and oils. Storage of these wastes at the site places the RFP in violation of the Resources Conservation and Recovery Act (RCRA) which is administered locally by the Colorado Department of Health by authority of the Environmental Protection Agency. Disposal of these wastes by conventional means is prohibited due to their radioactive contamination. The low level radioactive waste storage facility at the Nevada Test Site (NTS) will not accept these wastes due to their organic contamination. Supercritical CO2 is being evaluated as an extracting solvent to separate the organic compounds from the solid matrices. Surrogate wastes are being studied in the laboratory by spiking various solid substrates with organic solvents and oils and placing them in a supercritical CO2 extractor. The extraction vessel contents are sampled on line by gas chromatography in order to evaluate extraction efficiency. Whether this process will be scaled up to treat actual wastes so that they will be accepted by NTS depends largely upon the success of the laboratory scale extraction experiments.

68 **COMPARISON OF MEMBRANE AND CARTRIDGE SOLID-PHASE EXTRACTION FOR FIELD ISOLATION OF POLYCYCLIC AROMATIC HYDROCARBONS.**
Janece C. Koleis. Edward T. Furlong, and Paul M. Gates, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002.

Two solid-phase extraction (SPE) technologies, Emporel membranes (M-SPE) and IsoElute SPE cartridges (C-SPE), were tested to determine if they can be used as a simple, efficient, field-operable means for isolating microgram-per-liter to nanogram-per-liter quantities of polycyclic aromatic hydrocarbons (PAH) in 4- to 8- liter ground-water samples. The two technologies were compared using (1) reagent water fortified with 1.23 micrograms of individual PAH per liter, and (2) ground-water samples from a crude-oil-contaminated site near Bemidji, Minnesota. The M-SPE samples were collected and the PAH isolated at the wellhead. A separate, simultaneously collected C-SPE sample was field-processed in a mobile laboratory. In the laboratory, the SPE membrane or cartridge was extracted using dichloromethane and analyzed by gas chromatography-mass spectrometry with selected-ion monitoring. The authors observed acceptable recoveries for lower molecular weight PAH (Naphthalene to Pyrene) when using either C-SPE or M-SPE, with recoveries ranging from 56 to over 100 percent. M-SPE recoveries were superior for higher molecular PAH (Chrysene to Benzo(g,h,i)Perylene), from 18 to 56 percent compared to 2 to 33 percent for C-SPE.

[1] **Use of trade names in this abstract is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.**

69 A NEW MICROWAVE INSTRUMENT FOR RAPID SOLVENT EXTRACTIONS. **Todd Kierstead**
Robert Revesz, CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200

Liquid-solid extractions are among the oldest and most widely practiced sample preparation techniques for chemical analysis. They are performed on such diverse materials as plastics to determine additives, raw or processed foods to determine residual pesticides, and soils, sediments and tissue to measure the environmental impact of a variety of organic compounds. Frequently, the most time consuming steps in chemical analysis are these sample preparations. Microwave heating of organic solvents in closed containers can significantly reduce the extraction time required for the determination of many complex analytes. This paper presents data on priority pollutants in sediment and soils using traditional solvents with microwave extraction techniques. In addition, we have followed a more fundamental approach to improving extractability by selecting solvents with good dielectric properties. These approaches permit sample extraction times to be reduced from hours to less than 30 minutes. Studies have been conducted in microwave equipment specifically designed for safe operation using organic solvent extraction. The microwave heating system includes a specially designed solvent evacuation system to prevent solvent vapors from reaching their lower flammability limits. The system also includes a solvent vapor detection device and air flow switch designed to turn off the microwave power if solvent vapors are detected or no air flow is detected inside the microwave hearing cavity. To control extraction conditions a unique microwave transparent temperature sensing system is used to control the extraction temperature to within ±2° Celsius. These systems will be described and their advantages discussed.

406 MASS SPECTRAL CONFIRMATION OF DRUG RESIDUES IN TISSUE OF FARM-RAISED AQUATIC SPECIES. Sherri B. Turnipseed. Jose E. Roybal, Robert K. Munns, Heidi S. Rupp, David C. Holland, Austin R. Long, Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Denver, CO 80225-0087

As the aquaculture industry expands, efforts to monitor edible fish tissue for residues of drugs used to treat fungal and bacterial infection have increased. One aspect of this monitoring is developing methods to confirm drug residues determined by chromatographic analysis by a secondary technique, preferably mass spectrometry. Results from methods developed in our laboratory to confirm drug residues in aquatic species will be discussed. For example, particle beam LC/MS and GC/MS methods to confirm the presence of malachite green, a triphenylmethane dye used as a fungicide, and/or its long-lived leuco metabolite have been developed. The results from the analysis of fortified and incurred catfish tissue using these methods will be presented and compared. In another example, a multi-residue confirmation method for quinolones using GC/MS was developed and validated using catfish, salmon, and shrimp tissue.

70 **THE USE OF LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY FOR ENVIRONMENTAL ANALYSIS AT THE U.S. ENVIRONMENTAL PROTECTION AGENCY.** **Don Betowski. U.S. EPA, EMSL-Las Vegas, P.O. Box 93478, Las Vegas, NV 89193.**

The U.S. Environmental Protection Agency is interested in various environmental applications of liquid chromatography/mass spectrometry (LC/MS). Two applications are the determination of organic dyes and high-molecular-weight polynuclear aromatic hydrocarbons (PAHs) in environmental samples. Thermospray LC/MS has been successful in the analysis of samples for the detection of dyes. However, since thermospray LC/MS is a "soft" ionization technique, the spectra generated under this method are characterized by only a few ions. Consequently, little structural information is available from thermospray. Tandem mass spectrometric (MS/MS) techniques combined with thermospray can generate fragment ions that are structurally related to the parent compound. However, thermospray LC/MS without MS/MS can be used successfully in target analyses since the sensitivity to a variety of dye compounds is good. High-molecular-weight PAHs can be identified with particle beam LC/MS. A variety of sample extraction routines was used to recover many PAHs with molecular weights above 300 daltons from a contaminated soil. Particle beam LC/MS was used as the determinative step in the analysis of this soil. Instrument on-column detection limits as measured by selected ion monitoring were between 0.15 and 4 ng per compound. The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), prepared this abstract for a proposed oral presentation. It does not necessarily reflect the views of the EPA or ORD.

72 ULTRA TRACE ANALYSIS IN COMPLEX MATRICES BY NEW METHODS IN ENVIRONMENTAL ION TRAP MASS SPECTROMETRY, **William C. Schnute. Finnigan Corporation, 355 River Oaks Parkway, San Jose, CA 95134**

This paper will discuss the ways in which new Ion Trap technology can be applied to the identification and quantitation of trace level organics in various complex matrices. The ultra-sensitive nature of the Ion Trap allows processing of samples with concentrations in the parts per trillion level. Analysis of products meant for human consumption are generally complex in nature and require these low detection levels.

The additional use of MS/MS and negative ion techniques extend the range and capabilities of the Ion Trap. MS/MS simplifies the detection of suspected components in extremely complex matrices by eHminating interferences and co-eluting compounds. When combined with negative ion capabilities, the chromatographer can achieve extremely sensitive and specific detection of electrophilic compounds.

Examples of standards and samples (such as pesticides in foodstuffs and the products of micro-organisms in water supplies) will be presented showing the ultra-trace sensitivity and the expansion of dynamic range possible using these techniques.

73 FIELD COMPARISONS OF A WET EFFLUENT DENUDER AND FRIT METHOD WITH A FILTER PACK METHOD FOR THE MEASUREMENT OF NITRIC ACID AND PARTICULATE NITRATE

Susan M. Buhr, Fred C. Fehsenfeld, Richard B. Norton, and Robert E. Sievers
Aeronomy Laboratory, R/E/AL7.325 S. Broadway, Boulder, Colorado 80303

The measurement of nitric acid and particulate nitrate is of interest because these species are important components in tropospheric reactive nitrogen chemistry. It is desirable to have an automated method for the field measurement of particulate nitrate and nitric acid which is not labor intensive, and which minimizes gas and particle interactions. A method meeting these criteria has been developed using wet effluent technology. This method has been compared with the standard filter pack method at field sites in rural Alabama; Boulder, CO; and at Caribou, CO near the Continental Divide. The wet effluent denuder method has a sample frequency of 15 minutes and a detection limit of 10 pptrv **HNO3**. The method also provides a separate and simultaneous measure of particulate nitrate.

The nitric acid measurements agreed very well between the two methods, over the range of less than 0.1 ppbv to 4 ppbv. Particulate nitrate measured using the wet effluent system was much higher than that measured by the filter pack, and exhibited a strong diurnal variation. Principal component analysis indicates that the wet effluent particulate nitrate correlates strongly with photochemistry.

74 **THE ANALYSIS OF MARINE BIOTOXINS IN SHELLFISH.** **Eoin P. Carmody, Kevin J. James and Sean S. Kelly, Chemistry Department, Cork RTC, Bishopstown, Cork, Ireland.**

Dinoflagellate blooms (red tides) may produce biotoxins that cause paralytic shellfish poisoning (PSP) and diarrhetic shellfish poisoning (DSP). In Europe, a combination of monitoring of harmful algal blooms and determination of toxins levels is used by regulatory agencies to ensure shellfish quality. The use of pre- and post-column derivatisation with fluorometric HPLC for toxin analysis is outlined. Derivatisation using anthryl diazomethane(ADAM), bromoacetylpyrene (BAP) and other reagents are compared. DSP has only been recognised as a problem in recent years because of its similarity to bacterial enterotoxin poisoning. Diarrhetic toxins are polyether carboxylic acids (okadaic acid, dinophysistoxin 1 and 2) and are potent tumour promoters. To date, field measurements in shellfish cultivation areas show that substantial variations in toxin levels may exist both horizontally and vertically in the water column. For example, in Bantry Bay, Ireland, total diarrhetic toxin levels varied in a single day from zero to 6ug/g hepatopancreas (regulatory limit 0.8ng/g). Extensive sampling programs, ideally incorporating rapid screening methods for toxins, are therefore required to ensure public health in relation to shellfish consumption.

75 **THE DETERMINATION OF MERCURY IN ENVIRONMENTAL SAMPLES USING THE PERKIN-ELMER FLOW INJECTION MERCURY SYSTEM** **by S. MCINTOSH, J.BAASNER, C. HANNA - The Perkin-Elmer Corporation, 50 Danbury Rd.. Wilton, CT 06897-0219 and RANDY HERGENREDER. The Perkin-Elmer Corporation, 14818 W. 6th Avenue, Suite 6, Golden, CO 80401**

The determination of mercury in environmental samples is improved when the Flow Injection technique is used. A procedure for the determination of mercury in environmental samples using a dedicated Flow Injection Mercury System (FIMS) is discussed. The Flow Injection technique automates the generation of cold vapor mercury providing increased sample throughput with reduced sample and reagent consumption. The kinetic discrimination of the flow injection technique reduces interference effects commonly associated with the traditional batch method while also eliminating memory effects associated with the continuous flow method. The FIMS consists of a flow injection system integrated with a low pressure mercury source, an electrically heated quartz cell and a solar blind detector with optimum sensitivity at 253.7 nm. This compact system is completely controlled usinq an industry standard personal computer and advanced AA WinLab system software running under Microsoft Windows ' M. J\^Q analysis of environmental samples is performed using the EPA approved Flow Injection Method 245.1A, in which the generation of the mercury vapor is accomplished using the flow injection system. The mercury vapor is swept into the electrically heated quartz cell and the absorption signal is measured. The length of the absorption cell has been optimized to provide maximum sensitivity resulting in a detection limit of mercury in drinking waters of less than 10 ng/L Hg. This represents a 20 fold improvement in the mercury detection limit previously obtained with the FIAS system. Maximum sample throughput is obtained by coupling the FIMS with an autosampler resulting in a sample analysis rate equal to 120 determinations per hour.

76 AN INNOVATIVE FIELD SAMPLING KIT DEVELOPED FOR THE SPECIATION OF ALUMINUM IN NATURAL AND TREATED/DISTRIBUTED WATER USED FOR HUMAN CONSUMPTION. Jean-Charles Meranger. Denis G. Brule, and Belinda Lo, Health Canada, Environmental Health Centre, Tunney's Pasture, Ottawa, ON K1A 0L2.

A major objective of recent studies is on-site aluminum (Al) speciation in drinking water. An innovative kit was developed to differentiate between: 1) total (field acidified); 2) total weak-nitric-acid leachable (field-acidified/lab-filtered); 3) total dissolved (field-filtered/field-acidified); 4) dissolved monomeric (field-filtered/field-column-chelated/lab-acid-extracted) ; and dissolved organic complexes (field-filtered/field-column-chelation/field-acidified). A Sterifil-D vacuum filtration unit, with 0.45 sized pores in Triton-free esters of cellulose membranes, is used for field filtration. Ca-form Chelex 100 resin-filled columns are*prepared as follows: 200 grams of 100-200 mesh Na-form resin (Bio-Rad) are stirred for 3 hours in 1 L of 5 M HC1, and rinsed with deionized/distilled water. A 2 mL column bed of resin is formed, which is. converted to the Ca-form using a 2 N Ca solution, followed by rinsing with deionized/distilled water. On-site, a 50 mL sample percolates through the column at < 1 drop per second. Monomeric aluminum, extracted from the column resin with 1 N $HN0_3$, is determined by IC. Post-column reaction with pyrocatechol violet forms a complex, measurable at 580 nm using a UV/VIS Detector. Aluminum in the column extract is also measured by ICP-MS, as is aluminum in other samples.

77 DISINFECTION KINETICS IN DRINKING WATER. **Charles N. Haas, Mark S. Heath, Joseph Jacangelo, Uma Anmangandla, JoshJoffe, JoelC. Hornberger, Joseph dicker, and Ruth L. Hund. American Water Works Association Research Foundation,** 6666 **West Quincy Avenue, Denver, Colorado 80235.**

The recently promulgated Surface Water Treatment Rule (SWTR) requires a 3-log removal (99.9%) of *Giardia* cysts and a 4-log removal (99.99%) of viruses for drinking water treatment plants (WTPs). Up to 2-log removal can be credited through particle reduction via coagulation and filtration. The remaining microbial removal must occur using disinfection. Disinfection credit is determined by the CT product which is roughly defined as the product of the disinfectant concentration and the contact time. An inaccurate estimation of the CT required for disinfection could lead to the unnecessary design of new contact basins, increase in baffling in the contact basins, increase in the disinfectant dose, or inadequate disinfection. The USEPA has established CT tables which are used as guidelines for compliance with the SWTR. These tables are based on the Chick-Watson kinetic model of microbial inactivation. A bench and pilot scale study on real waters at the Portland Water Bureau determined that a more accurate disinfection model for *Giardia* disinfection is a modified Horn model which accounts for the decrease in disinfectant concentration during the time of contact. This study compares the CT required for disinfection using the modified Horn model and the CT tables established by the USEPA.

78 "ALMOST DIGESTIONS" or HOT-ACID LEACHES WITH CONTINUOUS FLOW MICROWAVE SAMPLE PREPARATION. Nancv Hoblack. Edward E. King, David Barclay, J. Douglas Ferguson, Lois Jassie, CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200

An important advance in sample preparation for atomic spectroscopic is the use of flow injection microwave digestion to produce a continuous flow microwave digestion. The approach automates the most time consuming portion of the analytical process: sample preparation. The SpectroPrep™ system embodies this hybrid technique and has been applied to environmental samples for preparation prior to atomic analyses.

79

ANALYSIS OF RADIONUCLIDES IN ENVIRONMENTAL SAMPLES BY ICP-MS,

Rob Henry, Fisons Instruments, P.O. Box 20460, Boulder, CO 20460-3460

The high sensitivity and element specificity of ICP-MS has been instrumental in the development of methods for the analysis of long lived radionuclides. A very high sensitivity interface has been developed which simplifies the analysis of environmental samples which have been prepared by preconcentration techniques. Examples of the sample preparation and analysis protocols will be described.

80 REGULATORY AND HEALTH ISSUES WITH THE UPCOMING ARSENIC DRINKING WATER REGULATION.

Bruce A. Macler. U.S. Environmental Protection Agency, Region 9, 75 Hawthorne Street, W-6-1, San Francisco, California 94105.

Ingestion of inorganic arsenic may lead to a variety of human health problems. Arsenic is known to be a human carcinogen (skin and internal cancers), as well as a cause of vascular disease and other adverse conditions. It occurs widely in both ground and surface source waters. There is thus reason to be concerned with potential health risks from arsenic in drinking water. EPA is in the process of revising the National Primary Drinking Water Regulation for arsenic, with an expected proposal date of November 1995. It is highly likely that the resulting Maximum Contaminant Level (MCL) will be substantially stricter than the existing MCL of 0.05 mg/liter. Because arsenic is a carcinogen, EPA policy directs that the arsenic Maximum-Contaminant Level Goal (MCLG) be zero. The SDWA further directs EPA to set the enforceable MCL as close to the MCLG as is feasible, based on availability of analytical methods and treatment techniques. Current analytical methods suggest a practical quantitation limit for arsenic in the range of 0.002 to 0.005 mg/liter. A variety of treatment techniques exist, although no Best Available Technology (BAT) has been established. While EPA has not proposed a MCL for arsenic, possible MCLs considered by EPA and others from this regulatory approach may be in the range of 0.002 to 0.005 mg/liter.

°1 RESULTS OF THE RECENT LOW LEVEL ARSENIC OCCURRENCE SURVEY IN CALIFORNIA,

M.W. Tikkanen. Association of California Water Agencies, 910 K Street, Suite 250, Sacramento, CA 95814.

Current work underway by the U.S. Environmental Protection Agency to revise the National Primary Drinking Water Regulation for arsenic has prompted many water agencies (particularly those in the arid southwest) to assess the impact of such a regulation. Lowering of the Maximum Contaminant Level (MCL) for arsenic to values between 1-20 ug/L has been suggested. However, little data is available on the occurrence of arsenic in water sources at levels below 5-10 ug/L.

In order to evaluate the impact of this regulation on California, and to assist the U.S. EPA in promulgating a drinking water regulation based on current, low level arsenic data, the Association of California Water Agencies conducted a survey that details occurrence of arsenic to a (reporting) detection limit of 1 ug/L. Samples from over 1400 ground and surface water sources were analyzed by GF-AAS or ICP-MS. Results of this survey, including analytical methods utilized will be presented.

ARSENIC OCCURRENCE IN U.S. WATER SUPPLIES. Michelle M. Frey, Marc A. Edwards, University of Colorado, Boulder, CO

In order to generate reliable occurrence data for low levels of arsenic, a national monitoring program was designed to support the development of the arsenic regulation through representational sampling of public water systems. Also included in the study was an assessment of trends in arsenic specie occurrence, e.g., As(III) and As(V), to assist municipalities in targeting appropriate removal technologies. The design criteria for the monitoring program incorporated the critical parameters required in extrapolating arsenic occurrence results to the compliance capability of public water suppliers. Common features that are likely to describe comparable water quality and impacts of treatment were identified for the population of PWSs. For purposes of this study, a group variable called Natural Occurrence Factor (NOF) was included in the design and analysis of the monitoring program. For each data record, a characterization string was assigned to include system size, population served, state, source type, and NOF. Statistical techniques assessing the comparability of occurrence patterns on the basis of the characterization string components were performed to identify the national tendency for arsenic occurrence within ranges considered for the future regulatory standard.

83 EVALUATION OF THE PRACTICAL QUANTITATION LEVEL (PQL) FOR ARSENIC USING ATOMIC ABSORPTION SPECTROPHOTOMETRY. A. D. Eaton, Montgomery Laboratories, 555 E. Walnut, Pasadena, CA 91101 and M.W. Tikkanen, Association of California Water Agencies, 910 K Street, Suite 250, Sacramento, CA 95814.

Considering that the maximum contaminant level (MCL) for arsenic is probably going to be lowered significantly, a study was done to assess the capabilities of laboratories for arsenic analysis in drinking water by atomic absorption spectrometry (both graphite furnace and hydride generation) at concentrations approximate to those being considered for the revised MCL.

The evaluation involved 22 laboratories and utilized four representative drinking water matrices to determine a practical quantitation level (PQL) for arsenic. Samples were spiked with arsenic at concentrations ranging from 1 to 10 ug/L. On an interlaboratory basis, analytical precision and bias changed significantly at concentrations < 4 ug/L, setting a lower limit to the PQL of 4 ug/L. This PQL could be used by the US Environmental Protection Agency in setting the revised MCL. Details of these analyses and results will be reported.

84 **ANALYTICAL CHEMISTRY OF ARSENIC IN DRINKING WATER.** **Jeffrey L. Oxenford. AWWA Research Foundation, 6666 W. Quincy Ave., Denver, CO 80235. Andrew Eaton, Montgomery Laboratories, 555 East Walnut Street, Pasadena, CA 91101.**

The Environmental Protection Agency (EPA) is considering lowering the maximum contaminant level (MCL) for arsenic in drinking water to a level between 1-10 ug/L. Detection limits using currently available techniques range between 0.5 - 5 ug/L and are therefore not sufficiently sensitive for compliance or to evaluate treatment effectiveness. Current methods also do not readily address speciation, which can play an important role in arsenic removal by treatment.

An ongoing project is addressing three techniques to improve the sensitivity and specificity for arsenic species in drinking water. These include: 1) hydride generation with cold trapping concentration followed by atomic absorption spectroscopy (AAS), 2) chelation solid phase extraction concentration followed by graphite furnace AAS, and 3) hydride generation concentration followed by inductively coupled plasma spectroscopy/ mass spectrometry (ICP/MS). Methods have been developed capable of speciating As (III) and As (V) with detection limits below 0.1 ug/L. An interlaboratory evaluation is being conducted on all three methods.

85 **SELENIUM MOBILIZATION BY IRRIGATION IN THE UNCOMPAHGRE RIVER VALLEY OF WEST-CENTRAL COLORADO.** K.C. Stewart. J.G. Crock, and R.C. Severson, U.S. Geological Survey, Box 25046, MS 973, Federal Center, Denver, CO 80225.

In 1986, the Department of the Interior (DOI) began field .investigations to identify the nature and extent of potential water quality problems that might be attributed to drainage from federally constructed irrigation projects in the Western United States. The DOI selected the Uncompahgre Project area (UPA) in western Colorado for a detailed study of geologic sources of selenium and its mobilization by irrigation because in the initial study high concentrations of selenium were found in stream sediments and water samples. A stratified random sampling design was used to assess selenium variation in soil and associated alfalfa among and within five geologic units described in the area. Based on analysis of variance (ANOVA), 57 percent of the variance in total soil selenium was accounted for by geologic units. By contrast, only 30 percent of the variance in water-extractable selenium was accounted for by geologic units. Selenium in soils ranged from 0.3 to 8.6 ppm. The geometric mean for all soils was 1.4 ppm—six times higher than the geometric mean of 0.23 ppm for soils of the Western United States. Soils derived from the Cretaceous Mancos Shale and its alluvium contained the highest concentrations—10 to 15 times greater than the mean for western soils. Selenium in alfalfa ranged from 0.03 to 9.5 ppm and showed a geometric mean of 0.33 ppm. The highest proportion of selenium variance in alfalfa was found at the smallest sampling interval, Analysis of variance, and the fact that selenium in alfalfa was most highly correlated with water-extractable selenium, suggests that mobilization and redistribution of selenium in the project area is enhanced by irrigation practices.

86 **SURVEY OF LEAD IN ENVIRONMENTAL MATRICES BY ATOMIC SPECTROSCOPY TECHNIQUES** ZOE A. GROSSER, The Perkin-Elmer Corporation, 50 Danbury Rd., Wilton, CT 06897-0219 and RANDY HERGENREDER. The Perkin-Elmer Corporation, 14818 W. 6th Avenue, Suite 6, Golden, CO 80401

Recent news has focused on the serious health effects of childhood lead exposure. Children up to the age of five years are particularly susceptible to neurological disruption because their brains are developing. Hence lead levels as low as 10 ug/dL in blood can cause behavioral difficulties and even loss in IQ. Adults may also be poisoned by lead and there is particular concern in industries such as lead smelting,, battery production, and radiator repair to ensure worker safety. Lead paint remediation and renovation of older structures may expose workers to hazardous levels of lead as well. Exposure to lead may come from many sources including paint, dust, soil, water, and buildings undergoing renovation. Analytical testing needs will grow with the lead remidiation industry. Lead surveys may be done with hand-held X-ray fluorescence units, but the bulk of lead determinations will be done in a conventional or transportable laboratory. Techniques such as graphite furnace atomic absorption (GFAA), flame AA, inductively coupled plasma optical emission (ICP-OES), and inductively coupled plasma-mass spectrometry (ICP-MS) will provide the capabilities required for environmental determinations. Lead determinations in paint (dried film and liquid), soil, and air will be required during remediation. Blood lead determinations are an important indication of exposure for both children and workers who may be exposed in high-risk industries. Regulations are being developed in both cases. Additionally, wastes generated during remediation may also have to be tested using the EPA toxicity characteristic leaching procedure (TCLP). Methods developed by various regulatory agencies for determining lead in a variety of matrices will be reviewed. Lead determination in paint, air, soil, and water will be described. The regulations governing blood lead determination and the practices employed will be outlines. We will examine the atomic spectroscopy techniques available for the determination and describe their strengths and weaknesses for different analytical scenarios.

87 APPLICATION OF GEOCHEMICAL MODELING TO PROPOSED METHODS OF DISSOLVED LEAD REMOVAL FROM A MINE DRAINAGE. Beth McMillan, Ronald W. Klusman, and Thomas R.Wildeman, Colorado School of Mines, Golden, CO 80401.

Geochemical computer modeling was applied to a mine sump water containing dissolved Pb^{+2} in excess of regulatory limits. The water was unusual because of a pH of 7.9 and alkalinity of 156 mg/L as CaC03 and yet the Pb^{+2} is 0.1 mg/L. MINTEQA2 was utilized for inverse modeling to determine the causes of the excess lead. Input parameters which yielded computed concentrations equal to the measured concentrations were determined in the inverse modeling. These parameters, including: pH, temperature, pressure and solids controlling the chemistry of the water, were considered to be the equilibrium conditions of the system. At equilibrium, the mass distribution of the dissolved lead was then determined. The Pb^{+2} was complexed primarily as soluble lead carbonate species and lead hydroxide species. From the mass distribution, treatment scenarios were configured and modeled. MINTEQAK was used to model possible treatment methods for removal of the dissolved lead. Aqueous CO_3^{-2} and OH- were added to drive the lead carbonate and lead hydroxide species to supersaturation causing precipitation of the solids. The model did not predict any change in the soluble lead concentrations. The lead carbonates and lead hydroxides remained undersaturated due to the buffered nature of the system. An alternative hypothesis of the addition of Fe^{+3} as FeCb was modeled. Ferrihydrite was formed and the lead was removed by adsorption to the oxyhydroxide. Results of modeling this system demonstrate geochemical modeling can be used as a tool to determine likely treatment methods for contaminant removal. However, field tests should be conducted to verify assumptions and to determine the effectiveness of geochemical modeling.

88 RECENT DEVELOPMENTS IN AND APPLICATIONS OF TWO DIMENSIONAL AND HIGH-FIELD ESR Jack H. Freed. Chemistry Department, Cornell University, Ithaca, New York 14853

The current status of two-dimensional Fourier Transform-ESR and of Far-Infrared ESR will be reviewed with recent examples from this laboratory. An important objective of this work has been the development of methods to study dynamic molecular structure in fluid materials and surfaces by modern ESR methods with enhanced resolution. It will be shown how 2D-ELD0R enhances resolution to both structure and dynamics in the study of complex fluids, and it also provides sensitivity to very slow motions. This has justified improved models of molecular dynamics which now include the details of a slowly relaxing local structure, whose dynamics can be very effectively separated from that of the (nitroxide)-probe molecule by 2D-ELD0R. The utility of FIR-ESR in conjunction with 9 GHz ESR for distinguishing related complex dynamics in glass-forming fluids and in polymers will also be discussed. The significant resolving power of FIR-ESR in distinguishing different radicals as' well as subtle differences in local sites in complex materials will be shown. The role of 2D-FT-ESR methods for solid-state structural studies in enhancing the accuracy and resolution of nuclear modulation patterns will be described.

89 PROBING STRUCTURE AND DYNAMICS IN PEPTIDES WITH SITE SPECIFIC ESR SPIN LABELING. Glenn L. Millhauser, Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064

Helical peptides serve as models for exploring the principles of protein folding. For the last several years our lab has been engaged in developing site specific spin label methodologies for probing structural transitions and local dynamics in these model helices. A particularly controversial finding using double labeling strategies, is that short helices follow the 3io-helix conformation and only longer sequences exhibit the expected geometry of a-helix. We are now finding the necessary sequence factors to stabilize a-helix in the shorter sequences. In related work, we are using spin labeled analogs of amyloid peptides in order to follow the progression of fibril formation which, in turn, is related to Alzheimer's and prion diseases. Finally, we are using 2D Heisenberg exchange spectroscopy to explore the early events of protein folding. An overview of these topics will be presented.

90 **"2+1" SECSY - A NEW VARIETY OF 2D PULSE ADJUSTING SPECTROSCOPY.**

A.Raitsimring*.R.H.Crepeau*.and J.H.Freed*.*) University of Arizona,Tucson, AZ 85721, +) Baker Laboratory of Chemistry, Cornell University,Ithaca, NY 14853.

A new variety of the 2D-pulse EPR technique called "2+1" SECSY is reported. This technique employed three pulses. Two of them, the first and third, generate the primary spin echo signal. The "+1" pulse, of fixed amplitude and width, is located between first and third pulses and the dependence of the spin echo shape (f coordinate measured from the end of the third pulse) on the "+1" pulse position, t, (second time coordinate) is investigated. The variable parameters are the amplitude and duration of the "+1" pulse. The adjustment of these parameters allows improvement of the spectral resolution and amplitude. We used the CrKCOQH), radical in irradiated monocrystals of malonic acid as a model system. We demonstrated that the amplitude of the spectral peaks is three to four times more than in SECSY (2D-2pulse) experiment after properly adjusting the variable parameters. The ability of "2+1" SECSY to suppress low frequencies and to reveal high frequencies in complicated ESEEM patterns was demonstrated using frozen DPPH solution in toluene. This feature of "2+1" SECSY is the opposite of standard ESEEM techniques which allow one to suppress higher frequencies. Direct calculations of thespin echo signal are in a good agreement with the experimental data. The applications of "2+1" SECSY to improve resolution of complicated ESEEM patterns is discussed.

91 **ANALYSIS OF ONE- AND TWO-DIMENSIONAL EPR SPECTRA IN THE SLOW-MOTION REGIME USING THE MODEL TRUST-REGION LEAST-SQUARES ALGORITHM**

David E. BudiL* Sanghyuk Lee, and Jack H. Freed, Baker Laboratory of Chemistry, Cornell University, Ithaca NY, 14850 and *Dept. of Chemistry, Northeastern University, Boston MA 02115

The dynamic parameters of a spin probe undergoing slow motion are most conveniently obtained from fitting model calculations based on the stochastic Liouville equation (SLE) to experimental spectra. The application of the "model trust region" minimization algorithm to the analysis of one-dimensional cw-EPR and multidimensional Fourier-transform (FT)-EPR spectra in the slow-motional regime will be described. The trust-region approach is inherently more efficient than the standard Levenberg-Marquardt algorithm, and the efficiency of the procedure may be further increased by a separation-of-variables method in which a subset of fitting parameters is independently minimized at each iteration, thus reducing the number of nonlinear parameters. These advantages, combined with recent improvements in the computational methods used to solve the SLE, have made it possible to carry out interactive, real-time fitting on a laboratory workstation with a graphical interface. Examples of fits to experimental data will be given, including multicomponent cw-EPR spectra and two- and three-dimensional FT-EPR spectra. Emphasis will be placed on the analytic information available from the partial derivative information utilized in the algorithm, and how it may be used to estimate confidence limits for the parameters, as well as the condition and uniqueness of the fit.

92 **LOW TEMPERATURE DYNAMICS OF A NITROXIDE SPIN-PROBE IN POROUS MATERIALS**

Claude Chachaty, DRECAM/SCM Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette cedex, FRANCE

The dynamics of the TEMPO radical in polar and non-polar solvents such as ethanol and methylcyclohexane adsorbed in porous inorganic glasses and crosslinked polymer resins has been investigated by X-band ESR between 100 and 250 K. The evolution of the lineshape with temperature has been analyzed by computer simulation of the spectra using a least-square fit method . Above the glass transition of ethanol (148 K), the spectra are significant of a partition of the spin-probe between the bulk and the solvent adsorbed on the pore walls whose fractions have been determined. The exchange rates between these microphases are found in the 10^{6} - 10^{1} s range for samples such as alumina where there is no hydrogen bonding between the probe and the OH groups of the adsorbent. When this bonding occurs, as in the case of silica samples, the exchange is inhibited or very slow, while the nitrogen hyperfine coupling constant becomes appreciably larger than in the free solvent (a_N = 16.9 G against 16.3 G). A limiting behavior is observed for the TEMPO radical in methylcyclohexane where this probe is completely adsorbed on the pore walls (a_N = 17.5 G). The temperature dependence of the exchange rate of the TEMPO radical in ethanol adsorbed on crosslinked poly-4-vinylpyridine resin is significant of a wide distribution of pore sizes, confirming our interpretations of nuclear relaxation experiments.

93 STUDIES OF TRANSIENT FREE RADICALS IN SOLUTION - LIMITATIONS AND ADVANTAGES OF ESR METHODS, by Keith A. McLauchlan, Physical Chemistry Laboratory, Oxford University, South Parks Rd., Oxford 0X1 3QZ, United Kingdom

This lecture will give an overall picture of the present state of the study of transient free radicals in solution using ESR and related methods. The advantages and disadvantages of continuous wave sampling methods and pulse methods, including FT methods will be described, and the reasons why the results from the two methods are nor always directly comparable will be discussed. Both methods suffer from the problem that it is only those radicals that survive the geminate period of radical reaction that are observed, and these may not be the first radicals formed in the system. Observations typically commence from 50 ns after radical formation, but before this time electron transfer, energy transfer, and radical substitution processes may occur but be invisible to the ESR experiment (although the CIDEP behaviour may be affected).

The major advantage of the ESR method lies in its spectral resolution which compares well with that of faster methods. However, the alternative techniques of Reaction Yield Detected Magnetic Resonance (RYDMR) and the study of the effect of Magnetic Field Effects (MFE) on radical reactions yield superior time-resolution, and they are interestingly complementary to the ESR methods in detecting precisely those radicals that react within the geminate period of the reaction. Examples will be given of radicals that may be detected using MFE, but not ESR, and of reaction processes detected by RYDMR, but not by ESR.

The MFE technique may be sensitive to radical concentrations far lower than are detectable using ESR, particularly in biological systems in which the concerted and amplificatory nature of the biochemistry can be exploited. The possibility exists for using extremely sensitive biological detectors (maybe even in ESR) to extend the concentration ranges of radicals that may be studied. This is at present an untouched technology, which has particular promise to the study of free radicals *in vivo*.

94 INVERSION-RECOVERY OF NITROXIDE RADICALS IN SOLUTION.

Nicholas J. Turro[1], Igor V. Koptyug[1,2]. and Stefan H. Bossmann[3], department of Chemistry, Columbia University, New York, NY 10027, USA; institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia; [3]Engler-Bunte Institute, University Karlsruhe, D-76128 Karlsruhe, Germany

In a conventional inversion-recovery experiment a non-uniform initial perturbation of a spectrum leads to a redistribution of magnetization across the spectrum thus obscuring the "true" recovery process. We overcome this problem by using two modifications of a standard experiment. In the first approach an almost uniform inversion is achieved by means of specially designed pulse-trains with excitation patterns which match the 3-line nitroxide ESR spectrum. In the second approach we essentially combine an inversion-recovery for the Mi=0 line with an analog of a pulsed ELDOR technique for Mi=±l lines, in a *single* experiment. This allows us to reconstruct the recovery of the *total* magnetization of the ensemble of radicals which is not affected by spin-diffusion. The spin-lattice relaxation times of several nitroxides are measured in different homogeneous and microheterogeneous environments. The Ti viscosity dependence in a "spinless" solvent CS2 is shown to be different from that in other solvents studied. This finding favors the recent conclusion that the interaction with a solvent contributes to the relaxation of nitroxide radicals.

95 PULSED AND CW EPR STUDY OF THE MOLECULAR MOTION OF A PHENALENYL SPIN PROBE IN CATION-EXCHANGED FAUJASITE ZEOLITES. **David C. Doetschman,[a] David Dwyer.[b] and Steven G. Utterback[c], [a]Department of Chemistry, S.U.N.Y., Binghamton, N. Y., 13902-6000, [b]Department of Chemistry, S.U.N.Y. at Brockport, Brockport, N. Y., 14420, and [c]Hostos Community College, Bronx, N. Y., 10451.**

The molecular motion of the phenalenyl (PNL) spin probe in the supercages of cation-exchanged X- and Y zeolites (faujasites) has been characterized by pulsed and continuous wave (CW) electron paramagnetic resonance (EPR). X- and Y-zeolites, whose cation sites were exchanged with the alkali metal ions, Li^+, Na^+, K^+, Rb^+, and Cs^+ were examined. A correspondence between the temperature dependences of the PNL electron spin phase memory time and the CW EPR spectrum has been observed. Both display evidence of a low temperature thermal activation from a stationary (non-rotating) molecular state to a state of in-plane rotation. The rotation appears to be about an axis along which the half-filled, non-bonding *it* orbital on the PNL probe interacts with an exchanged cation in the supercage. This interaction has been characterized by a correlation between the CW EPR spectrum of the stationary molecular state and the nuclear hyperfine frequency of the exchanged cation. Both CW and pulsed EPR spectra of the PNL probe also show a higher temperature activation from the in-plane rotating state to an effectively isotropic state of rotation in which the PNL-cation bond is thought to be broken.

96 ANOMALOUS TEMPERATURE DEPENDENCE OF TETRAHEDRAL COBALT(II) ELECTRON SPIN RESONANCE IN ALUMINOPHOSPHATE-5 MOLECULAR SIEVES„ Vadim Kurshev and Larry Kevan, University of Houston, Department of Chemistry, Houston, TX 77204-5641.

As-synthesized aluminophosphate-5 containing cobalt(II) [CoAP0-5] is blue and after calcination it becomes yellow-green. This has been previously interpreted as a valence state change from Co(Il) to Co(lII)„ This apparent valence change was supported by a severalrfold decrease in the electron spin resonance (ESR) of Co(ll) at 4 K. New ESR work verifies this intensity change at 4 K but shows no change at 20 K! The anomalous change in ESR intensity with temperature can be fully understood in terms of the energy level structure of cobalt(II) in a crystal field of tetrahedral symmetry. Thus, the complete ESR temperature dependence directly indicates cobalt(II) framework incorporation into tetrahedral sites and no oxidation of Co(Il) to Co(lII) in CoAPO-5 upon calcination.

EPR STUDIES OF ION-EXCHANGED ZEOLITES. **Sarah C. Larsen. Adam Aylor, Alexis T. Bell and Jeffrey A. Reimer, Department of Chemical Engineering, University of California, Berkeley, and Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720**

Ion-exchanged zeolites, such as copper ZSM-5 and cobalt ferrierite, exhibit high catalytic activity for the direct decomposition and selective catalytic reduction, respectively, of nitric oxide. Although the ion-exchange level can be correlated with catalytic activity, little is known about the structural environment of copper and cobalt in these materials. We have used EPR spectroscopy to probe the local structure of copper and cobalt sites under various conditions of oxidation, reduction, and hydration. In situ EPR experiments on samples exposed to nitric oxide at room temperature and at elevated temperatures were also performed. The results provide insight into catalyst structure, thermal stability, and chemical reactivity.

Application of ESR to Study the Hydrogenation of Alkenes and Benzene over a supported Pd Catalysts

Albert Carley,[a] Hywel Edwards,[a] Fred E. Hancock,[b] S. David Jackson,[b] Brvnmor Mile.[a] M. Wyn Roberts[3] and Christopher C. Rowlands[3]

a School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, P.O. Box 912, Cardiff CF1 3TB. b ICI Katalko, R & T Group. Billingham, Cleveland.

ESR has been rather neglected by the catalyst community despite it being the most sensitive hniaue available for detecting free radicals and paramagnetic metal ions, which are intermediates nardcipants in many catalytic processes. In this paper, we describe its application to the detection °f paramagnetic intermediates on the surface of a palladium catalyst during heterolytic hvdrogenation reactions. ESR, in conjunction with spin trapping, is shown to provide a convenient, tomle technique for detecting surface adsorbed hydrogen atoms from the room temperature dissociation of molecular hydrogen on an alumina supported palladium catalysts (< 0.04% Pd). By using D2 we have also been able to demonstrate directly the occurrence of hydrogen/deuterium spillover on to the alumina surface by H/D atom transfer to surface hydroxyl groups. Alkyl and aromatic free radical intermediates formed by reaction of the H« atoms with alkenes and benzene have also been detected on a catalyst surface for the first time.

99 **AN INVESTIGATION OF STABLE FREE RADICALS IN POLYIMIDES USING 250GHz ESR SPECTROSCOPY.** **Myonq K. Ahn, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809; Mary Ann Meador, NASA Lewis Research Center, Cleveland, Ohio; David E. Budil, Keith A. Earl, Joe Moscicki, and J. H. Freed, Department of Chemistry, Cornell University, Ithaca, New York 14853**

High-performance polyimides such as PMR-15 are used in applications requiring high temperature stability. These polyimides produce room temperature electron spin resonance (ESR) spectra from stable free radical species formed upon exposure to temperatures above 573K. The thermo-oxidative degradation involves free radicals in the presence of oxygen gas. The X-band ESR spectrum gives a nearly symmetric single narrow peak. The intensities at different temperatures suggest the presence of at least two free radical species. In this work . we demonstrate the usefulness of the high-field (250GHz) electron spin resonance spectrometer (HFESR). The first derivative HFESR spectra of PMR-15 and PMRII samples show the composite of two powder patterns consisting of two resolved g^y and partially resolved g± peaks, which unambiguously demonstrate the presence of the two free radical species.

100 **EPR EVIDENCE FOR BINDING OF CUPRIC ION TO MAX.** **William E. Antholine[a]. Chakravarathy Narasimhan[b], Kent W. Wilcox[c], Hongbing Wang[b], and Timothy Herman[b], [a]Biophysics Research Institute, and Departments of [b]Biochemistry and [c]Microbiology, Medical College of Wisconsin, Milwaukee, 53226-0509**

The MAX. protein is a member of the basic region-helix loop helix-leucine zipper family of specific DNA binding proteins. Two MAX monomers dimerize and bind to the palindromic CANNTG binding site. MAX can also bind as a heterodimer with oncoprotein c-Myc. Myc activates transcription of genes believed to regulate cell proliferation and differentiation. A cupric ion binding site on a MAX homodimer has *gy* =2.26 and *A y* =167 G. Titration experiments indicate a single cupric ion binding site per MAX homodimer. A shift f° ^1 ⁻2.24 and *Ay* =175 G is observed for Cu-MAX bound to oligonucleotide. It is argued that a pair of nistidine residues at position 81 in the leucine zipper domain of the MAX homodimer facilitate the binding of cupnc ion to MAX. (Supported by NTH grants CA-22184 and RR01008, and Falk Medical Research Trust rund).

101 REACTION OF DIOXYGEN WITH THE NITRIC OXIDE ADDUCT OF FERROUS BLEOMYCIN BOUND TO DNA. **M. Claire Kennedy,[a] William E. Antholine[b], Qunkai Mao[c], and David H. Petering[a], department of Biochemistry, and [b]Biophysics Research Institute, Medical College of Wisconsin Milwaukee, 53226, and [c]Department of Chemistry, Univ. Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201**

The configuration of an NO complex of ferrous bleomycin is altered if ON-Fe(U)Blm is bound to DNA (1). Addition of air to ONFeBlm-DNA completely removes the ONFeBlm-DNA signal within about 10 min *(h/2* min). If excess NO is present, the decrease of ON-FeBlm-DNA is slower, presumably because of the reaction of excess NO with 0_2. The rate of decrease of the ONFeBlm signal is much faster (t_m ~ 1 min) in the absence of DNA. One product of the reaction is Fe(UI)Blm DNA, as indicated by the concomitant increase in the low-spin EPR signal for the species. A second product in the absence of DNA is nitrite, NO^. No detectable levels of nitrate are found. An intermediate in this reaction may be peroxynitrite. Formation of peroxynitrite is consistent with the observed products, but so far, strand breaks have not been detected. **(Supported by NIH grants CA-22184 and RR01008, and ACS grant DHP-31)**

1. **Antholine, W. E., and Petering, D. H. (1979)** ***Biochem. Biophys. Res. Common.*** **91, 528-533.**

102 SATURATION RECOVERY EPR OF A MUTANT OF NITROUS OXIDE REDUCTASE. **S. Pfenninger[a], W. E. Antholine[a]. C. C. Felix[a], J. S. Hyde[a], P. M. H. Kroneck[b], and W. G. Zumft[c]. [a]Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, 53226, [b]Univ. Konstanz, Konstanz, FRG, and [c]Univ. Karlsruhe, Karlsruhe, FRG.**

The enzymes, nitrous oxide reductase (N_2OR) and cytochrome *c* oxidase (COX), have a mixed valence [Cu(1.5)...Cu(1.5)], 5=1/2 site instead of a monomeric Cu_A site (1). Both of these mixed-valence sites have unusually fast relaxation. Temperature-dependent saturation-recovery data for the binuclear mixed-valence site in a mutant of N_2OR, which has two coppers per monomer instead of the four coppers per monomer found in the wild type, are similar to data for the mixed-valence sites in both wild type N_2OR and COX. It is concluded that the unusually fast relaxation is mtrinsic to the mixed-valence configuration. The relaxation rate varies from $T^{3,3}$ to T^{3-8} for the slower rate to T^{3-7} to $T^{4,3}$ for the faster rate. The saturation-recovery curves for the mutant are fit to at least double-exponential curves. A five-fold dilution of the sample does not alter the saturation-recovery data. Cross relaxation and superposition of spectra do not contribute to the results. Results are discussed in terms of allowed and forbidden transitions, T_1 distributions due to strain, and effects of inhomogenous lines. This work is supported by NSF grant DMB9105519.

1. **Antholine, W. E., Kastrau, D. H., Steffens, G. C. M., Buse, G., Zumft, W. G., and Kroneck, P. M. H.,** ***Eur. J. Biochem.*** **209, 875-881 (1992).**

103

ACTIVATION OF ALPHA-HUMAN TUMOR NECROSIS FACTOR(TNF-a) BY HUMAN MONOCYTES (THP-1)EXPOSED TO 2-CHLOROETHYL ETHYL SULFIDE (H-MG) .**Carmen M. Arroyo,** Robert L. **Von Tersch, Commander, U.S.A. MRICD, ATTN:SGRD-UV-DA/Carmen M. Arroyo/ APG-EA, MD 21010-5425.**

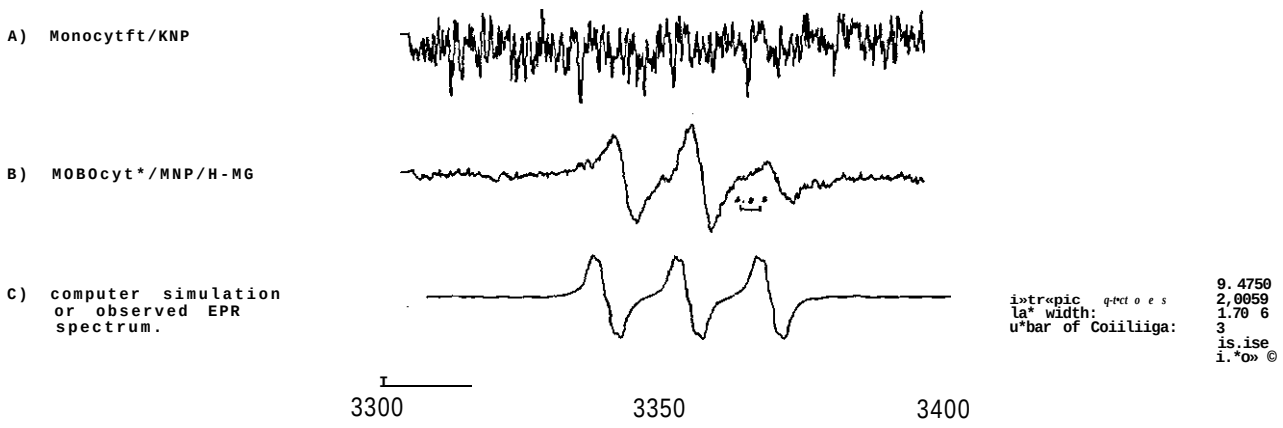
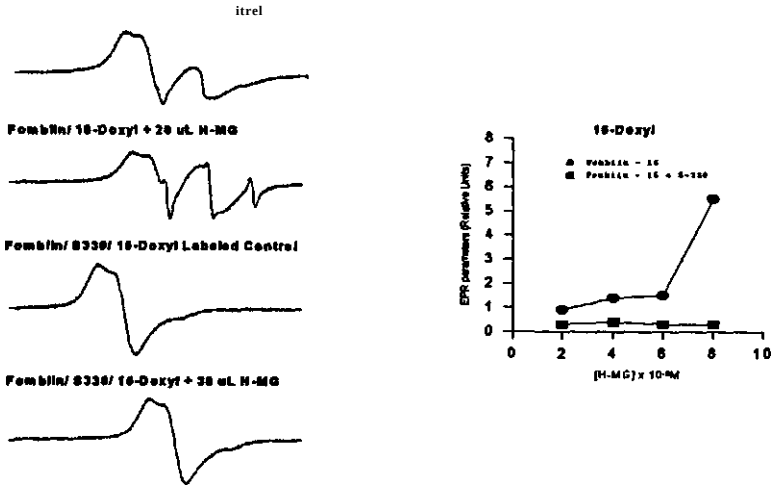


Figure 1: Typical EPR/HKP adduct detected vben human monocytes were exposed to H-MG

Tumor necrosis factor (TNF-a) is a monokine produced by monocytes and macrophages in response to different stimuli. To determine whether vesicant agents such as half-mustard gas (H-MG; chemical structure. $ClCH_2CH_2SCH_2CH_3$) induce the release of TNF-a in human monocytes (THP-i), ELISA experiments were conducted at different post exposure.times. The results from these studies are as follows: 1) Significant increases m the TNF-a concentrations (pg/mL) were observed as a function of time when THP-1 cells were exposed to 100 of 2 M H-MG. 2) Furthermore, this laboratory detected the generation of free radicals using EPR/bpm Trapping techniques. In particular, spin adducts of 2-metnyW-nitrosopropane (MNP) were observed (Figure 1) suggesting protein degradation by-products after exposure to H-MG. The involvement ot a serine protease activity in the cytotoxic action of TNF has been reported. Therefore TNF-a may play a role as a biochemical marker for pathophysiological changes induced by H-MG or related agents.

104

EPR/SPIN LABEL TECHNIQUE AS AN ANALYTICAL TOOL FOR DETERMINING THE RESISTANCE OF REACTIVE TOPICAL SKIN PROTECTANTS (rTSPs) TO THE BREAKTHROUGH OF VESICANT AGENTS.**Carmen M. Arroyo, Commander,U.S.A. MRicn ATTN: SGRD-UV-DA/ Carmen M. Arroyo, APG-EA, MD, 21010-5425.**



The rate of reaction of vesicant agents with the nitroxide group of spin probes intercalated in rTSP multilayers has been studied to examine the mechanism of lateral diffusion. Four N-oxyl-4-4*-dimethyloxazolidine derivatives of stearic acid, 5-NS, 7-NS, 12-NS and 16-NS were used as spin probes. Ointment formulations (rTSPs) based on perfluorinated polyether (PFPE, i.e. fomblin RT-15) were prepared and spin labeled. The spin labeled vehicle, fomblin-RT-15 and vehicle containing chloroamide (S-330, an anti-vesicant) were exposed to various concentrations of the vesicant agent. The rate of reaction as determined by the order parameter (S) was dependent on the depth of penetration of the paramagnetic group into the vehicle (fomblin) and on the chemical composition of the reactive anti-vesicant under investigation. The net change of the viscosity of the vehicle and the chemical composition were seen to affect the penetration profile. This will provide a useful, in vitro screening technique to develop anti-vesicant TSP's.

105 EPR STUDY OF POINT DEFECT PRODUCTION IN VITREOUS SiO_2*

Wm. R. Austin and Robert G. Leisure, Dept. of Physics, Colorado State University, Fort Collins, CO 80523

The production of defects in high purity silica by x-rays and y-rays is being studied by electron paramagnetic resonance. Measurements of the EPR signal due to the E' center, a radiation induced paramagnetic oxygen vacancy, are made as a function of ionizing radiation dose. An experimental technique to maintain reliable dose calibration while varying the photon energy distribution from conventional metal anode x-ray sources has been developed. Irradiations at photon energies in the 5 to 50 keV x-ray region are compared with 7-ray exposure at 660 keV. Experimental results and implications concerning models for the defect production mechanism will be presented.

***Research supported by Office of Naval Research; Contract No. N00014-91-J-1607 (G.B. Wright).**

ELECTRON SPIN ECHO MODULATION SPECTROSCOPIC EVIDENCE FOR FRAMEWORK

106 SUBSTITUTION OF Ni(l) IN NiAPSO-11. Naoto Azuma, Chui Wee Lee and rry Kevan, University of Houston, Department of Cheinsitry, Houston, Texas 77204-5641.

The various Ni(I) species formed by reduction and adsorbate interactions in •licoaluminophosphate-11, synthesized by incorporation of Ni(ll) in the synthesis ture (NiAPSO-11) and formed by partial ion exchange of Ni(l) by Ni(ll) (NiH-SAPO-ll) studied recently for the first time by electron spin.resonance (ESR). Significant differences in the ESR parameters between NiAPSO-11 and NiH-SAPO-ll for nickel coordination to methanol, carbon monoxide and ethylene adsorbates indicate that Ni(l) is in dif:Eerent: s l t e s in these two materials and suggests that Ni(l) in NiAPSO-11 is in a framework site. This has been confirmed here by electron spin echo modulation data on these synthesized and ion-exchanged materials„ Analysis of the deuterium modulation from deuterated methanol and ethylene adsorbates gives different coordination geometries for the synthesized and ion-exchanged nickel-incorporated SAPO-11 materials and is consistent with Ni(l) being in a framework site in NiAPSO-H.

107 AN EPR STUDY OF THE STRUCTURE OF SURFACE BOUND SURFACTANT AGGREGATES INVOLVED IN SHEAR FLOCCULATION

Martin G. Bakker, Dexter D. Murphy, Terry Clark, Brandon Davis, Department of Chemistry, The University of Alabama, Tuscaloosa, Al 35487-0336 and D. R. Spears, U. S. Bureau of Mines, Tuscaloosa Research Station, Tuscaloosa, Al.

Shear Flocculation is a process in which aggregation of fine (micron sized) particles with adsorbed surfactant, is produced by applying a shear force to an otherwise stable suspension. The mechanism of this process is poorly understood, and this process, despite a number of advantages is not widely used. In order to determine if surface bound surfactant aggregates are important in the flocculation process hexadecyltriammonium bromide (HTAB) with an attached spin-label was synthesized. The presence of the spin-label was found to produce only minor changes in the flocculation behavior. EPR Spectroscopy shows clearly the presence of surfactant aggregates. As the flocculation process proceeds, the mean particle size increases, and the proportion of the surfactant present in an aggregated form increases. Changes in the shear force during flocculation produce changes in the mean particle size which are mirrored by changes in the ratio of aggregated to non-aggregated surfactant. The implication of these observations on the mechanism of shear flocculation and the structure of surface bound surfactant aggregates will be discussed.

108 CONTINUOUS WAVE AND SPIN ECHO EPR SPECTROSCOPY OF Mn^{2+} IN *ras* p21 WITH ^{17}O LABELING AT 5 T.

Brendan F. Bellew. Christopher J. Halkides, Gary J. Gerfen, Robert G. Griffin, Alfred G. Redfield, and David J. Singel. NW14, MIT, Cambridge, MA 02139.

***ras* p21 is a guanine nucleotide binding protein that plays a vital role in the regulation of cell growth and differentiation. The protein acts as a molecular switch, undergoing structural changes critically coupled to the divalent metal-nucleotide binding site. High frequency (139.5 GHz) EPR spectroscopy of Mn^{2+} in p21 is used to characterize the *solution* structure of this binding site— specifically to probe for coordination with ^{17}O labeled water and [^{17}O-3]threonine. Using a Spectral Subtraction Method patterned after Reed & Leyh *(Biochemistry,* 19, 5472 (1980)) we determine hydration numbers of four in the GDP- and two in the GTP-form of the protein, and estimate an average ^{17}O hyperfine coupling of -7.7 MHz. In samples prepared with [^{17}O-3]threonine, a putative ligand in the GTP-form, we ascertain an ^{17}O hyperfine coupling of -2.8 MHz. In all of these experiments, the elevated frequency leads to a critical reduction in Mn^{2+} EPR linewidth, which enhances the sensitivity of the linewidth to ^{17}O hyperfine broadening. The implications of these EPR and complementary X-band ESEEM results (Halkides *et al. Biochemistry,* 33, (1994)) for the mction of p21 will be discussed and compared with models based on X-ray crystal structures.**

109 **POWDER ENDOR STUDIES OF DEUBSTITUTED 1,4-NAPTHOSEMIQUMONES.** **Chris Bender and Gerald T. Babcock.** ***Department of Chemistry, Michigan State University, East Lansing, MI 48824.***

We have examined he anisotropic hyperfine interactions of 'H nuclei with the unpaired spin density distributed throughout the aromatic skeleton of 2,3-disubstituted-l,4-napthosemi-quinones, some of which are participants in biological redox processes. This is part of an ongoing study with the aim of characterizing the powder ENDOR spectral properties of quinoid and phenoxy radical intermediates. Overlapping powder ENDOR lines have been resolved by specific deuteration of the quinones' substituent groups, and a McConnell-Strathdee analysis of the dipolar hyperfine tensor for each set of equivalent protons has been used to map spin density on nuclei not probed by a direct nuclear coupling. Further studies of neighboring group effects on the tunnelling rotation of substituents is underway.

110 **SPECTROSCOPIC STUDIES OF THE CHARGE-TRANSFER REACTIONS OF STRONG ELECTRON ACCEPTORS AND LECITHIN** **Chris Bender,** ***Department of Molecular Pharmacology, Albert Einstein College of Medicine, 1300 Morris Park Avenue, Bronx, NY 10461.***

Charge transport at biological membranes can be mimicked and examined in an electrochemical cell partitioned by a lipid bilayer membrane, which is analogous to cells used to study the Interface between Two Immiscible Electrolyte Solutions (ITD3S). An otherwise insulating membrane can be rendered conducting by doping the lipid solution (from which the membrane is formed) with electron acceptors that form charge-transfer complexes with the lipid. In a previous study, free radicals were trapped in the lipid solution, although no correlation to conductivity nor aid in identifying the charge carrier was apparent[1]. Further study, reported here, provides kinetic and analytical data that implicate proton and possibly electronic charge carriers among the several dopants.

[1]C.J. Bender and H.T. Tien, J. Electroanal. Chem., 284, 1990, 217.

111 **NEW PULSE EPR SPECTROMETER OF UNIVERSITY OF ARIZONA.**

P.Borbat. A.Raitsimring .Department of Chemistry, University of Arizona,Tucson, AZ 85721.

A pulsed EPR homodyne or superheterodyne spectrometer operating at 8-18 GHz has been constructed at the Department of Chemistry of the University of Arizona. The spectrometer operates with two independent mw-channels and allows up to four pulses per channel. The pulse width is >3ns, pulse power is up to lkW. Each of the pulses may be programmed as x,-x,y or -y. One of the channels is switchable to second frequency. This method of pulse setting allows two and three pulse trains, "2+1" pulse sequence, double electron-electron resonance and HYSCORE. The first experiments investigating the nuclear environment of Mo(V) in LMo'0* (L= hydrotis (3,5-dimethyl-l-pyrazolyl)borate) and low spin iron(III) in porphyrins will be reported.

We thank NSF (BIR-9224431) for financial support.

-M 2 MAGNETIC RESONANCE STUDIES ON THE WATER EXCHANGE RATE OF GADOLINIUM BASED CONTRAST AGENTS: MODULATION OF CHEMICAL EXCHANGE DUE TO BINDING ON HUMAN SERUM ALBUMIN. **T. E. gofers, N. V. Tsekos, J. H. Hwang, R. B. Clarkson, R L. Belford, Noyes Laboratory, 505 S. Matthews, Urbana,'II61801.**

Both the Solomon-Bloembergen-Morgcn (SBM) model and chemical exchange theory show that an important factor which determines the overall Proton Relaxation Enhancement (PRE) effect in MRI contrast agents (CA) is the rate of the water exchange between the bulk water and the first coordination sphere of the compound. Studies of the magnetic field dependence (Nuclear Magnetic Resonance Dispersion [NMRD] studies) of the PRE effect of a lipophilic contrast agent in HSA indicate that the water exchange rate is lower than in aqueous solutions.^{17}0 NMR studies of contrast agents based on the paramagnetic lanthanide ion Gadolimum(nT) (Gd^) were conducted to investigate the temperature dependence of the water oxygen's transverse relaxation time. These studies can provide direct indications on the range of the water exchange rate as well as approximate values of the pertinent thermodynamic quantities (enthalpy and entropy of the exchange process). A model adapted from the work of Swift and Connick *et al* was employed to fit the temperature dependence of the nuclear transverse relaxation of the available contrast agents. This model was then used to understand the corresponding data for a lipophilic contrast agent, Gd-EOB-DTPA, in both aqueous and HSA solutions. The water exchange rate obtained from our^{17}0 NMR results is in agreement with the corresponding rate values obtained from the NMRD experiment. **Partial support for this work was provided by the NIH (RBC, GM42208).**

113 DELOCALIZATTON OF UNPAIRED ELECTRONS IN ACCEPTOR-BRIDGE-DONOR MOLECULAR STRUCTURES AS MONITORED BY EPR SPECTROSCOPY. **R. Krzyminiewski*, A. Bielewicz*, J. Kudynska** and H.A. Buckmaster**. ""Institute of Physics, Adam Mickiewicz University, 65614 Poznan, Poland. **Department of Electrical and Computer Engineering, University of Victoria, P.O. Box 3055, Victoria, B.C., V8W 3P6, Canada.**

This poster reports the first application of EPR spectroscopy to study the degree of electron derealization in acceptor-hydrogen bridge-donor molecular bridges created by different substitutional acid groups in the organic molecule piperidine. EPR measurements were made at 290 K on polycrystalline samples which were y-irradiated with doses up to 150 kGy. Measurements were also made on UV irradiated frozen organic solvent solutions at 77 K. It was found that increasing the electronegativity of the hydrogen bridge causes a significant decrease in the nitrogen hyperfine interaction which implies that a significant increase in the degree of delocalization of the unpaired electrons has occurred. Measurements were also made on irradiated stilbene to study the role of an acceptor-rc bridge-donor. Different asymmetric substitutional groups can be used to remove the centrosymmetry of stilbene and create an optically active nonlinear molecule. Such studies can evaluate the potential of using organic molecules as the active material in molecular electronics.

114 EXPLORATORY 9 GHZ CW-EPR OXIDATION STUDIES OF SELECTED COMMERCIAL MOTOR OILS. **J. Kudynska and H.A. Buckmaster. Department of Electrical and Computer Engineering, University of Victoria, P.O. Box 3055, Victoria, B.C., V8W 3P6, Canada.**

The possible application of 9 GHz CW-EPR to study the oxidation processes that occur in commercial motor oils has been initiated. The objective was to determine whether EPR could be used to study those factors that contribute to the breakdown of the various lubricating oils used in the crankcases of gasoline and diesel fueled engines. This poster reports the results of the first stage in this evaluation. Four commercial motor oils were oxidized at 100 °C and 200 °C temperatures for varying time intervals. It was found that the free radical concentration increased at significantly different rates in these oils and that this increase was greatest in the oils from one manufacturer. This implies that the latter were more susceptible to temperature induced oxidation and would have shorter lifetime under normal crankcase operating conditions.

115 LOW TEMPERATURE OXIDATION KINETICS OF AN HV BITUMINOUS COAL As STUDIED BY DYNAMIC *IN SITU* 9 GHz CW-EPR SPECTROSCOPY. J.Kudynska anc H.A. Buckmaster. Department of Electrical and Computer Engineering, University of Victoria, P.O. Box 3055, Vjctoria, B.C., V8W 3P6, Canada.

This is the first report that information concerning the free radical species that are involved in the low temperature oxidation of coal can be obtained using CW-EPR spectroscopy. It is shown using an Alberta foothills hv bituminous coal that the Arrhenius diagramatic analysis of dynamic *in situ* 9 GHz CW-EPR can be used to calculate "activation" energies which characterize the various reaction stages in the low temperature oxidation process. It was found that coal behaves differently when subjected to dry air and nitrogen gas flow. The most evident thermal feature is the existence of two and three linear regions for coals subjected to dry air and nitrogen gas flow, respectively. The two regions with positive Arrhenius slopes for the latter are similar to those for the former gas. The third region with a negative Arrhenius slope appears in the temperature interval 293-323 K and was correlated with decomposition of peroxygen radicals. The "activation" energies in this region depend on the initial moisture content of the coal samples. The initial positive slope region has much larger Arrhenius slopes than the second higher temperature region when the samples are subjected to dry air and nitrogen gas flow. Hydroperoxygen decomposition reactions appear to dominate in the former region which create other free radicals and produce primarily gaseous oxidation products whilst the reactions in latter region produce solid oxidation products with much lower activation energy values.

116 EPR, ENDOR AND ESEEM STUDIES ON THE RIESKE IRON-SULFUR PROTEINS OF BENZENE DIOXYGENASE

Jasvinder K. Shergill, Clive S. Butler, Stephen Seah, Andrew C. White, Jeremy R. Mason and Richard Cammack *Centre for the Study of Metals in Biology and Medicine, King's College, University of London, Campden Hill Road, London W8 7AH, U.K.*

Benzene dioxygenase catalyses the conversion of benzene to ci's-benzene dihydrodiol. The *Pseiidomonas putida* enzyme is a three-component system, comprising a flavoprotein and a ferredoxin (Fd), which transfer electrons from NADH, to an iron-sulfur protein (ISP) containing a Rieske-type [2Fe-2S] cluster and a catalytic iron centre. The ISP consists of two dissimilar subunits arranged in an *a2fil* configuration. We have cloned all of the components of the system in *E. coli,* and expressed them separately and together. The *bedCl* gene, which encodes the a-subunit, was expressed to high levels, so that it represented 80% of the soluble protein. Well-resolved EPR, ENDOR and ESEEM spectra of the [2Fe-2S] clusters of the Fd and ISP components have been obtained with the cell-free extracts from recombinant *E. coli* cells. ESEEM spectra showed that the ligand environment of the Rieske-type cluster comprises two strongly-coupled histidine nitrogens. The cluster in the Fd component showed similar coordination by two nitrogens. The results indicate the Fd is also a Rieske-type protein, although its EPR spectra and redox potential are not typical. ENDOR showed the presence of proton couplings to the iron-sulfur clusters to exchangeable and non-exchangeable protons. Sequence-specific mutagenesis of the Fd was carried out, to investigate the ligands to the cluster. Mutation of the proposed histidine ligands prevented insertion of the cluster. Mutations to neighbouring amino acids caused subtle modifications of cluster geometry.

117 REDUCTIVE NITROSYLATION OF OXO-CHROMTUM(V) BIS(2-ETHYL-2-HYDROXYBUTYRATE) BY HYDROXYLAMINE, by Lenny M. Carruthers. Christina L. Closken, Surendra N. Mahapatro, Department of Chemistry, Regis University, Denver, Colorado 80221, and Sandra S. Eaton, and Gareth R. Eaton, Department of Chemistry, University of Denver, Denver, Colorado 80208.

Reaction of hydroxylamine with oxo-chromium(V) bis(2-ethyl-2-hydroxybutyrate) produces two primary products that can be separated by ion exchange chromatography. The products were assigned as Cr(I)nitrosyls on the basis of magnetic susceptibility and *JR.* data (Gould et al., Inorg. Chem. 1983, *22,* 971). To more fully characterize the chromium centers, the products were examined by EPR. In aqueous buffer, pH 3.0 to 3.5, both species have fluid solution g values of 1.969 and a nitrogen hyperfine splitting of 6.2 G. In frozen buffenglycerol solution the g values are g^=1.993, gj = 1.915. These g values are characteristic of a system with a single unpaired electron in the dxy orbital, consistent with formation of a $Cr(NO)2^{+}$ moiety that can be represented as {CrNO}^.

COMPUTER ASSISTED ESR STUDY OF THE ORDERING AND DYNAMICS OF DOXYLSTEARIC PROBES IN ASYMMETRIC PHOSPHOLIPID BILAYERS. Claude Wolf, URA CNRS 524, CHU St. Antoine, 27 rue de Chaligny, 75012 Paris, Claude Chachaty, DRECAM/SCM, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette, France.

Dhatidylcholines with chains of variable unequivalent lengths have been prepared by chemical 1°lion of the natural egg ^phosphatidylcholine, yielding 74% palmitoyl and 26% stearoyl residues •[acyc]sition 1. Position 2 was alternately esterified by decanoic (PC10). lauric (PC12), myristic (PC14) and '[n] Mtic (PC 16) acids. The lamellar phases formed by these phospholipids have been studied by X-ray Sactiori and ESR of doxylstearic spin-probes (5NS & 16NS). For PC 10 and PC 12, the X-ray patterns h w the existence of two homogeneous phases : an interdigitated and a non-interdigitated lamellar [s] ° [es] b[e]|ow and above the gel ->• fluid phase transition (T_c), respectively, whereas the ESR displays two-component spectra in a wide temperature range above T_c. This is significant of the coexistence of two gel and/or fluid phases where the order parameters and mobility of the nitroxide probe are different. A similar behavior is observed in the case of PC 14, with an additional weakly ordered phase at the vicinity of T_c. Several computer programs have been designed for the automatic fit of the spectra using a least-square procedure, which provide a reliable determination of component fractions, order parameters and reorientation correlation times as well as of exchange rates among the coexisting phases.

119 CONSTRUCTION OF A CYLINDRICAL "RIBBON-WOUND" EPR Q-BAND CAVITY. Wenqe Wang and N. Dennis Chasteen, Chemistry Department, Universityof New Hampshire, Durham, New Hampshire 03824

Robust yet sensitive Q-band (35 GHz) cavities are needed, for routine variable temperature EPR measurements down to 2 K. Such cavities must withstand repeated temperature cycling as well as provide high microwave energy density and magnetic field modulation at the sample. We have designed a TE_{011} cylindrical cavity consisting of a brass ribbon imbedded in an epoxy/quartz composite. This cavity has all the advantages of the traditional silver wire-wound cavity often used for Q-band measurements but is much more robust and easier to construct. The cavity suppresses degenerate resonant modes and minimizes eddy currents induced by field modulation. With Varian Q-band modulation coils, a 100 KHz modulation field of 27 G peak-to-peak is obtained at the sample. The cavity Q, S/N with weak pitch, and modulation penetration are comparable to those obtained with either a wire-wound cavity or a cavity constructed with a thin silver wall on a epoxy/quartz substrate. No background signals are observed. Details of construction of the brass ribbon-wound cavity will be presented.

120 A SINGLE CRYSTAL EPR AND ESEEM ANALYSIS OF CU(H)-DOPED BIS(L-HISTIDINATO) CADMIUM DIHYDRATE.

Michael J. Colaneri and Jack Peisach, Dept. of Molecular Pharmacology, Albert Einstein College of Medicine, 1300 Morris Park Ave., Bronx NY 10461

A study was undertaken to investigate the nature of the hyperfine and quadrupole coupling parameters of the distant ^{14}N in Cu(II)-coordinated histidine imidazole in the titled complex to further our understanding of the ESEEM patterns obtained for copper proteins. Single crystal EPR data have been measured in order to obtain accurate g and Cu(II) hyperfine tensors. EPR spectra rich in ligand hyperfine structure were observed in ^{63}Cu-doped crystals grown from D_2O. From these spectra, approximate hyperfine couplings for two ^{14}N nuclei have been deduced as well as partial couplings associated with two "1=1/2" interactions. The hyperfine and quadrupole tensors of the remote ^{14}N m the Cu(II)-ligated imidazole have been determined from single crystal ESEEM measurements and can be compared to those previously obtained in Cu(H)-doped L-histidine HC1 H_2O. The present ESEEM study shows that a single imidazole coordinates to the Cu(II). From these results, a Cu(II) binding site is postulated whereby the metal ion 'gates to only one histidine molecule. Further support for this model comes from the room temperature measured & and Cu(II) hyperfine tensors, which appear to each be the average of a pair of symmetry related tensors measured K. The tensor averaging at room temperature is believed to occur by the Cu(II) ion hopping between adjacent nistidme binding sites.

121 TWO DIMENSIONAL FOURIER TRANSFORM ESR APPLIED TO LIPID DISPERSION SAMPLES-EXPERIMENTAL ADVANCES . Richard H. Crepeau. Sunil Saxena, Sanghyuk Lee, Bald Patyal and Jack H. Freed, Department of Chemistry, Cornell Universitv^ Ithaca, New York 14853 y*

Advances in instrumentation in our FTESR spectrometer have now made possibl detailed studies of model membrane dispersions in the presence of excess water. With the reduction of instrumental dead times to below 50 ns the short relaxation times of dispersion samples are no longer a problem. High repetition rate signal averaging with time resolution better than 1 nsec allows data collection of the rapidly decaying signals with a good signal to noise ratio. Corrections for pulse width and phase interaction between successive pulses have permitted us to reduce minimum pulse separation times and enhance the signal strength and quality within the short decay times characteristic of the dispersion samples.

Advances in nonlinear least squares fitting procedures now allow objective extraction of information from the 2D experimental spectra. The 2-D format of the data in a 2 pulse experiment allows easy separation of the homogeneous and inhomogeneous T contributions. The three pulse ELDOR experiments allow separation of relaxation processes into Heisenberg exchange and electron-nuclear dipolar interactions providing detailed information of the structure and dynamics of the model membranes.

"IN-SITU" EPR ANALYSIS OF HYDROGENATED CARBON THIN FILMS

Mark Hoinkis and Mark Crowder, IBM, 5600 Cottle Rd, San Jose, CA 95193.

We report on "in-situ" EPR studies of amorphous hydrogenated carbon films. A thin film deposition system is adapted to an EPR system so that deposited thin films can be transferred to an EPR cavity under vacuum deposition conditions. This allows EPR observation of thin films prior to exposure to atmosphere and directly after deposition. Amorphous hydrogenated carbon thin films were prepared by DC sputtering a graphite target using an argon/hydrogen plasma. The resultant amophorous hydrogenated carbon film has an EPR signal which is stable in vacuum, but undergoes a large irreversible reduction when exposed to atmosphere. To probe the loss of the EPR species, carbon samples were prepared in vacuum and then exposed to various gas conditions. Oxygen gas causes a reversible[4]- and irreversible loss of the EPR signal intensity. The extent of the EPR signal decrease is dependent upon the deposition conditions used to prepare the carbon film, and in some cases an irreversible reduction of approximately 70% of the "in situ" EPR signal were detected.

1. M. Hoinkis, et. al., Applied Physics letters 61, 2653 (1992).

123 QUANTITATION OF COAL AND DIESEL SOOT BY HIGH FREQUENCY (W-BAND) EPR SPECTROSCOPY. Naresh Dalai[1]. Alex I. Smirnov[2]. and R. Linn Belford[2]-[3], department of Chemistry, West Virginia University, Morgantown, WV 26506-6045, and [2]Illinois EPR Research Center, College of Medicine and [3]Department of Chemistry, University of Illinois, Urbana, IL 61801.

There is an urgent need for quantitative experimental methodology to analyze diesel soot-coal particulate mixtures. Mixtures of coal dust with diesel soot from machinery are often formed during mining, creating an extremely hazardous environment. Since both coal and diesel soot contain free radicals, EPR can be used in analysis of such mixtures. We have explored the EPR methodology using as examples a diesel soot (sample I), an B3C-101 (Illinois #6) coal (sample H), and their mixtures. At X-band (9.5 GHz) both samples have single-line EPR spectra with only slightly different g-values: (gr&i)[=10"3]- Therefore, the EPR signal from a coal-soot mixture cannot reveal the difference between two radical types present. In contrast, at W-band frequencies (94.5 GHz) the g-value resolution is increased by a factor of 10, and this allows us to separate the EPR signals from different mixture components. The results provide a basis for development of a sensitive, quick, and reliable method for analysis of coal/soot mixtures based on high frequency EPR spectroscopy. N.D. thanks the US Bureau of Mines for support (Gl 135142). This work used the resources of the Illinois EPR Research Center (NTHP41-RR01811).

124 RESOLUTION OF OVERLAPPING SPIN LABEL SPECTRA BY CW SATURATION PROVIDES ACCESS TO THE DEPTH PROFILE OF LIPID-PROTEIN INTERACTIONS.

. ^ Dalton and Keith W. Miller, Dept. Biological Chemistry and Molecular Pharmacology Harvard Medical School, and Dept. Anesthesia, Massachusetts General Hospital, Boston, MA 02114.

The loss of integrated intensity in the partially saturated V, EPR signal relative to the h nturated control was used to quantify the saturation transfer (a) deriving from changes in su t'on of doxyl nitroxide reporters at various depths in the membrane. The calibration of a with "'°rientational motion was performed using 5-doxylstearic acid bound to albumin in a Medical Advances **loop gap resonator, analogous to the use of hemoglobin by Squier and Thomas (Biophys. T 49921 (1986)) for the TE_{102} cavity. EPR spectra of the acetylcholine receptor (AcChoR) econstituted into one lipid milieu, dioleoyl [C18:lA9cis] phosphatidylcholine (DOPC) with doxyl r -Qhgg,t postions 5,6,9,12,14 and 16 on stearic acid, consisted of a composite of motionally restricted nrobes adjacent to the protein (boundary) and more mobile probes in the bulk lipid. At 0°C the boundary probes at C-5, 6 and 9 possessed long correlation times (30 < x < 65 us) with noticeable retardation of motion at the C-9 unsaturation position whereas *x* was shorter (2-3 fold less) below the double bond. Trends were compatible with observations on the DOPC liposomes alone and with previous studies of the A9 *trans* unsaturated lipid (Dalton and Miller, Biophys. J. 65:1620 (1993)).**

125 ESEEM SPECTROSCOPY OF ^{15}N REMOTE NITROGENS IN Cu^{2+}-(IMIDAZOLE^ AND SUPEROXIDE DISMUTASE. **Sergei A. Dikanov[9'10], Andrei P. Spoyalov[3], Isabella Felli , Maria-Silvia Viezzoli , Jiirgen HUttermann[c], institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia, Department of Chemistry, University of Florence, 50121 Florence, Italy,^ 'Biophysics Department, Saarland University, 66421 Homburg (Saar), Germany, Present address: Battelle, Pacific Northwest Laboratory, Macromolecular Structure & Dynamics, Richland, Washington 99352.**

Orientationally-selected ESEEM spectra from remote ^{15}N nuclei of a Cu^{2+}-(imidazole)$_4$ complex have been obtained in the microwave frequency region 9.12-9.82 GHz. Conditions corresponding to the singularities in the fundamental nuclear transitions were reached in this region. The development of these lineform singularities in orientationally-selected spectra is discussed. The knowledge of the magnetic fields corresponding to the singularities was used to find the hyperfine couplings for the remote nitrogen as a=2.44 MHz and T=-0.39 MHz as well as to determine the angle between the axis of the complex and the direction of largest principal tensor element as 40°. The hyperfine couplings with remote nitrogens of histidine ligands of copper ion are also determined by ESEEM study of ^{15}N substituted Superoxide dismutase (SOD). The part of remote nitrogen nuclei in SOD has hyperfine couplings close to those in the Cu -(imidazole)$_4$ complex. The second part has smaller isotropic constant a=l.l MHz due to different orientation of imidazole planes relative to the metal ion.

5 ORIENTATION DEPENDENCE OF ELECTRON SPIN LATTICE RELAXATION RATES FOR NITROXYL RADICALS AND CHROMIUM(V) PORPHYRINS IN FROZEN SOLUTION, **Jine-LongDu. Rachel I. Konda, Sandra S. Eaton, and Gareth R. Eaton, Department of Chemistry, University of Denver, Denver, CO 80208**

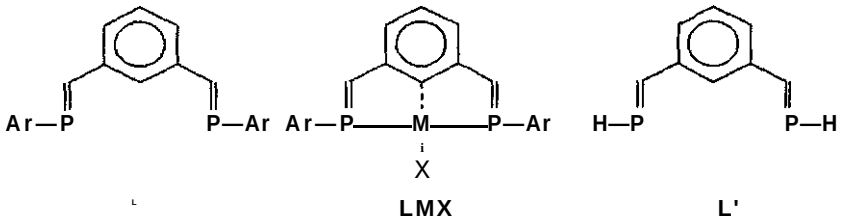
Electron spin lattice relaxation rates, 1/Ti, were measured by saturation recovery for mtroxyl radicals in a series of solvents and for nitridochromium(V) tetratolylporphyrin and nitrido chromium(V) octaethylporphyrin in toluene or 9:1 toluene.tetrahydrofuran. At 100 K the relaxation rates for the nitroxyl radicals increased with decreasing polarity of the solvent. In each solvent the relaxation rates were orientation dependent with the slowest rates observed when the magnetic field was parallel to the molecular z axis (the axis of the nitrogen p-orbital containing the unpaired electron). Deuteration of the solvent or the nitroxyl had negligible impact on the relaxation rate. The relaxation rates for the two Cr(V) porphyrins were similar to each other and faster than for the nitroxyl radicals. Rates were faster in the perpendicular plane (the porphyrin Plane) than normal to this plane.

127 250 GHZ EPR STUDIES OF POLARITY GRADIENTS ALONG THE ALIPHATIC CHAINS IN PHOSPHOLIPID MEMBRANES, **Keith A. Earle. Josef Moscicki, Mongtao Ge, David E. Budil, and Jack H. Freed, Baker Laboratory of Chemistry, Cornell University, Ithaca, NY 14853**

Rigid limit 250 GHz EPR spectra have been studied for a series of phosphatidylcholine spin labels («-PC where *n* = 5,7,10,12,16) in pure dispersions of dipalmitoyl phosphatidylcholine (DPPC) and l-palmitoyl-2-oleoyl phosphatidylcholine (POPC) as well as dispersions of DPPC containing the peptide gramicidin-A (GA) in a 1:1 molar ratio. The greatly enhanced g-tensor resolution of250 GHz EPR permits a careful study of the nitroxide g-tensor as a function of spin probe location and membrane composition. In pure lipid dispersions, as the spin-label is displaced from the polar head group, A_{zz} decreases and increases as they assume values typical of a non-polar environment, appropriate for the hydrophobic alkyl chain region. In the presence of GA, A_{zz} and depend only weakly on label position, and are characteristic of a polar environment. These results may reflect increased penetration of water into the alkyl chain region of the lipid in the presence of GA. The spectra from the pure lipid dispersions also exhibit a broad background signal that is most significant for 7-, 10-, and 12-PC, and is more pronounced in DPPC than in POPC. It is attributed to spin probe aggregation yielding spin exchange narrowing. The addition of GA to DPPC essentially suppressed the broad background signal observed in pure DPPC.

128 • EPR STUDY OF THE ELECTROCHEMICAL REDUCTION OF A DIPHOSPHAALKENE CHELATING AGENT AND OF ITS PALLADIUM AND PLATINUM COMPLEXES. **Michel Geoffrey, Abdelaziz Jouaiti, Gustavo Terron and Gerald Bemardinelli. Department of Physical Chemistry, University of Geneva, 30 Quai Ernest Ansermet, 1211 Geneva, Switzerland.**

The ESR spectra of the radical anion (L~) have been obtained by electrochemical reduction of a solution of diphosphaalkene (L) in THF at 200K. Due to the presence of the two P=C bonds, three isomers are expected for (L) : EE, EZ/ZE and ZZ. Although these three rotamers were distinguished by ^{31}P-NMR of the neutral molecule, they led to the same ESR spectrum after electrochemical reduction. *Ab initio* calculations on (L') show that, at room temperature, the ESR spectrum probably results from a rapid exchange between the 16 isomers due to a rapid rotation around the P=C and C (phosphaethyiene)-C (benzene) bonds. The frozen solution spectrum is also discussed. (L) is shown to act as a terdentate ligand for Pd(II) and Pt(II) ions. It is shown by ESR that the reduction of this complex is a ligand based process. The unpaired electron is mainly delocalized in a ligand %* orbital, the contribution of the metal d orbitals is revealed by the g anisotropy measured in frozen solution.



L LMX L'

129 High Frequency (139.5 GHz) EPR Investigation of Short Alanine-Based Peptides in Aqueous Solution.

Gary J. Gerfen.[1] Gary V. Martinez,[2] Glenn L. Millhauser,[2] Robert G. Griffin,[1] David J. Singel.[3]
[1]Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139. [2]Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064. [3]Department of Chemistry, Harvard University, Cambridge, MA 02138.

Small peptides (<20 amino acids) are emerging as effective tools in the study of protein structure and dynamics. Recently, it has been demonstrated that short alanine peptides containing 16 or 17 residues readily form helices in aqueous solution. The introduction of nitroxide methanethiosulphonate spin labels (MTSSL) via Cys residues has allowed EPR spectroscopy to be used in the investigation of these folded peptides. Pulsed and cw EPR spectroscopy at 9 GHz has yielded extensive information on motions with conelation times of ~10^{-9} s or less. In order to enhance spectral sensitivity to faster motions (TR ~lf>^{10} s) and to motional anisotropy, studies of the 16-mer peptide 3k 11 (with the MTSSL attached to a Cys at position 11) in aqueous solution have been performed at 139.5 GHz, 5 Tesla. Analysis of high frequency spectra taken from 0° to 24° C (sample size 20 picomoles) reveals anisotropy in the nitroxide motion which cannot be detected in 9 GHz data. The effects of this motional anisotropy on the determination of correlation times and on the interpretation of peptide folding pathways is discussed.

ELECTRON SPIN RELAXATION OF IRRADIATED FUSED QUARTZ AT FOUR FREQUENCIES, **Barnard Ghim, Susanne Pfenningert, Richard W. Quine, Gareth R. Eaton, and Sandra S. Eaton, Departments of Chemistry and Engineering, University of Denver Denver, Colorado 80208 and tBiophysics Research Institute, Medical College of Wisconsin, Milwaukee, Wisconsin.**

Electron spin relaxation time measurements were performed on a sample of irradiated fused quartz at L-band (1.2 GHz), S-band (3 GHz), C-band (5.9 GHz), and K-band (19 GHz). T and T_m were measured by saturation recovery and electron spin echo, respectively. At each microwave frequency the values of *T*\ were about 50% longer when the magnetic field was along the z axis of the g-tensor then in the xy plane. There was little dependence of T^ on microwave frequency. Values of T_m measured at L, S, C, and X-band as a function of pulse turning angle extrapolate to T2 = 24±1 usee at small turning angle, independent of microwave frequency.

131 **SPIN TRAPPING HYDROXYL RADICALS GENERATED BY IONIZING RADIATION IN THE TUMOR OF A LIVING MOUSE WITH VERY LOW FREQUENCY EPR.** **H. J. Halpern. C. Yu, E. Barth, M. Peric and G. M. Rosen, University of Chicago, 5841 S. Maryland Ave., Chicago, IL. 60637 and University of Maryland, 20 N. Pine St., MD. 21201**

It is widely believed that hydroxy! radicals produced by water radiolysis are responsible for the toxicity of ionizing radiation in tissues. Indirect hydroxyl radical assays in living tissues are highly qualitative; they are prone to a variety of artifacts. Direct measurements of hydroxyl radicals evolved by radiation in the leg tumor of a living animal has been accomplished using low-frequency electron paramagnetic resonance in combination with spin trapping. These hydroxyl radicals produced by ionizing radiation are detected in the tissues and tumor where they evolve nearly time coincident with their evolution. To our knowledge, this is the first report of such a direct measurement of radical evolution in the tissues a living animal. These initial measurements have required very high doses of radiation (3000 Gy). It provides the most direct proof of the widely believed evolution of hydroxyl radicals in tissues in response to high dose ionizing radiation. Measurements of hydroxyl radicals generated by ionizing radiation in cellular systems fail to elucidate higher level homeostatic responses to this and other oxygen derived toxins. Measurements with improved sensitivity are possible. They should allow more precise dissection of the toxicity mechanisms of ionizing radiation in tissue.CA-50679, HL-33550, DCB-8616115.

132 **ANISOTROPIC SPIN LATTICE RELAXATION TIMES - [3Fe-4S]$^{1+}$ FERREDOXIN FROM *GIARDIA DUODENAUS*.** **Stephen M. Townson[a], Graeme R. Hanson[b], Jacqueline A. Upcroff, Peter Upcroff, Y.C. Zhongf and John R. Pilbrow*. 'Queensland Institute of Medical Research, The Bancroft Centre, Brisbane, Qld, 4029, Australia. [b]Centre for Magnetic Resonance, The University of Queensland, St. Lucia, 4072, Australia, department of Physics, Monash University, Clayton, 3168, Australia.**

Oxidised (as isolated) [3Fe-4S]$^{1+/0}$ ferredoxin from the protozoan parasite *Giardia duodenalis* exhibits an orthorhombic (S=l/2) EPR spectrum ($g_{xy<z}$=1.9500,1.9799,2.0210; 2 K) typical of [3Fe-4S]$^{1+}$ cluster containing metalloproteins. A variable temperature (2-18 K) EPR study of this signal reveals dramatic changes in the linewidth and spectral lineshape. The spin lattice relaxation times have been determined from saturation recovery experiments performed as a function of magnetic field and temperature. The results reveal anisotropy in the spin lattice relaxation time which changes as a nrnction of temperature. The origin of the anisotropy and temperature dependence of Tj will be discussed in terms of the current spin coupling model and previous EPR and magnetic susceptibility results for the [3Fe-4S]$^{1+}$ cluster in *Desulfovibrio gigas* ferredoxin II.

133 **MULTIFREQUENCY EPR STUDIES OF MONONUCLEAR AND BINUCLEAR COPPER(II) PATELLAMIDE COMPLEXES AND THE IMPORTANCE OF MAGir ANGLES.**

Anna L. van den Brenk[a], Graeme R. Hanson[b], Lawrence R. Gahan[a], Cliff J. Hawkins[b]. "Department of Chernistry and the [b]Centre for Magnetic Resonance T? University of Queensland, Qld., Australia, 4072.

Patellamide D (patH^), a marine cyclic octapeptide from the asddian *Lissoclinum patella,* with two oxazoline and two thiazole rings, has the 24-azacrown-8 macrocyclic structure. Multifrequency EPR has identified multiple mononuclear ([Cu(patH$_3$)D and three binuclear ([Cu$_2$(patH$_2$)]$^{2+}$, [Cu$_2$(patH)(OH)]$^+$ and [Cu$_2$(patH$_2$)(C03)]) copper(II) patellamide D complexes. The copper(II) ions' coordination sphere involves three nitrogen atoms, arising from a deprotonated amide, oxazoline and thiazole rings. While the EPR spectrum of [Cu$_2$(patH$_2$)(OH)]$^+$ and [Cu$_2$(patH$_2$) (CO3)] are typical of dipol$_e$-dipole coupled binuclear (S=l) copper centres, the spectrum arising from [Cu$_2$(patH$_2$)]$^{2+}$ is typical of two mononuclear (S=l/2) centres. The lack of dipole-dipole coupling is attributed to the relative orientation (defined by the angles £ and n) of the two copper(II) centres rather than the distance between them. The magnitude of the angles 54.7° and rj, 45.0°, determined by computer simulation, correspond the so called "magic angles" used in solid state NMR to essentially eliminate dipole-dipole coupling, ie. the diagonal elements (J^JyyJ^) of the exchange coupling tensor are zero.

134 **THE ACTIVE SITE OF HYDROXYLAMINE OXIDOREDUCTASE: EVIDENCE FROM INTEGER-SPIN EPR FOR A NEW METAL CLUSTER IN PROTEINS.**

Michael P. Hendrich. Michael Logan, Dave M. Arciero, Kristoffer K. Andersson, John D. Lipscomb, and Alan B. Hooper, Department of Biochemistry, University of Minnesota, Minneapolis, MN 55455.

Hydroxylarnine oxidoreductase (HAO) from *Nitrosomonas europaea* catalyzes the oxidation of NH$_2$OH to NO2". The enzyme contains 8 hemes per subunit (MW 63 kDa) which participate in catalytic function and electron transport. In the resting ferric state of the enzyme, we find that these hemes can be categorized on the basis of new EPR data as follows. Four are non-interacting, ferric c-type hemes. Two hemes are low-spin and weakly spin-coupled through an interaction which is approximately dipolar on the basis of frequency-dependent g-values. The final two hemes are low-spin and exchange-coupled; this cluster is the origin of a **new integer-spin EPR signal which can be quantitatively associated with the active site of HAO. This resonance vanishes upon addition of substrates or cyanide, or with inactivation of HAO by** H2O2. **For reduced HAO,** a **different, new integer-spin EPR signal is observed from this active site, which is composed of** a **high- and low-spin fercous heme. The enzymatic site of HAO thus contains a metal cluster of a type not previously observed in proteins.**

135 **A HIGH FREQUENCY CW AND PULSED EPR SPECTROMETER BASED ON AN X-BAND INTERMEDIATE FREQUENCY**

P. Hofer, K. Holczer*, M. Kloza and D. Schmalbein, Bruker Analytische Messtechnik, 76287 Rheinstetten, Germany and ""University of California, Los Angeles

The g-factor resolution enhancement and the gain in sensitivity for small samples makes high frequency EPR attractive for a manifold of applications in biology, chemistry and physics. As diverse the applications are as high are the demands on flexibility in experiments and operating frequency. A most general approach to high frequency EPR is therefore an intermediate X-band frequency design where the majority of the microwave transmitter and receiver system is allready existing. The advantages are especially evident in pulsed EPR where the pulse shaping, pulse phase-setting and quadrature detection is independent from the actual EPR working frequency. As an initial step we have developed a 94 GHz accessory which can be attached to the ESP 300E (CW) or the ESP 380E (FT) EPR spectrometer. The first CW and pulsed EPR results obtained with this set-up are presented.

136 ELECTRON AND NUCLEAR SPIN RELAXATION EFFECTS IN PULSED ENDOR SPECTROSCOPY

p Hofer, Bruker Analytische Messtechnik, 76287 Rheinstetten, Germany

In a pulsed ENDOR experiment nuclear spin polarization is created by a selective microwave pulse. This Dolarization decays with the electron spin lattice relaxation time T_{1e}. It is therefore necessary that the whole pulse sequence consisting of preparation, polarization transfer and detection is shorter than T_{1e} in order to obtain an ENDOR spectrum. However, the process of sweeping the RF through the nuclear spin transition does not only result in the ENDOR spectrum. It also creates a new state of nuclear spin polarization which has different relaxation properties than the polarization before the RF pulse. It requires now relaxation via the forbidden EPR transitions to reach thermal equilibrium. The slowly relaxing polarization components can be measured by a second, delayed read-out RF pulse. It is shown by theory and experiments that an ENDOR spectrum can be obtained even at a time $t >> T_{1e}$ after the initial microwave preparation pulse. Application of this pulse sequence to disordered systems results in an ENDOR spectrum with better resolved turning points. Furthermore, a narrow spectral hole appears at the nuclear Larmor frequency, providing a B_0-field calibration with very high precision.

137 SOLVENT EFFECTS ON THE g ANISOTROPY OF SEMIQUINONE RADICALS: EPR AT VERY HIGH FREQUENCY.

A. Jain. M. J. Nilges and R. L. Belford, Illinois EPR Research Center, University Of Illinois, 506 S Mathews, Urbana, IL 61801

Very high frequency EPR (95GHz) spectra of semiquinone radicals in frozen solution are reported. At this frequency, the increased Zeeman interaction readily resolves the anisotropic components of the g-matrix. The radical-solvent interactions are important in understanding the structural variations in the g-matrix. We have used a variety of solvents, both polar and nonpolar, to generate semiquinone radicals from various quinones and have measured the g-anisotropy. For the most part, the hyperfine splittings remain unresolved, even in deuterated solvents. Comparison of the g-matrix of semiquinone radicals in different solvents is quite important and hydrogen-bonding has been known to play a remarkable effect on specific components of the g-matrix. Thus the role of hydrogen bonds during the semiquinone radical formation is of particular importance to understand their formation in *in-vivo* systems. There are consistent trends in the variation of the components of the g-matrix with respect to nature of the solvents and structure. These trends can be understood in the light of SCF-MO (both *ab initio* and semi-empirical) calculations of the g-tensor. This work was supported by a research resource grant from NTH (P41-RR01811).

138 CHEMICAL AND HEISENBERG EXCHANGE IN ION PAIR SOLUTIONS REVISITED BY T\a DIMENSIONAL EPR SPECTROSCOPY S. Kababva. Z.Luz and D.Goldfarb, Chemical ph ° Department Weizmann Institute of Science, Rehovot, Israel 76100.

The dynamic processes in tetrahydrofuran (THF) solutions of 2,5-di-t-butyl-p-benzoquinone, Na^+ (DtBPBQ- ja + ion-pairs, have been studied by two-dimensional (2D) exchange Fourier transform (FT) EPR spectroscopy. Measurem ^ were made at room temperature (17-20° C) on solutions with radical concentrations ranging from 4.5 10"[5] to 3 5 IQ-JW and with mixing times varying from 0.3 jos to 6 p.s. Analysis of the EPR spectra indicate the presence of two tvn DtBPBQ" ,Na^+ ion-pairs which are labeled A and B. In both species there is intramolecular Na^+ hopping but while ' ion-pair A the process is slow and suitable for monitoring by the 2D exchange method, in ion-pair B it is much faster !! results in a selective smearing out of some of the hyperfine lines. In the 2D spectra characteristic cross peaks due to Na^+ hopping and Heisenberg exchange (HE) appear. Analysis of these spectra provide information about title intramolecular Na^+ hopping rate in ion-pair A, $k_{£_E}$, as well as on the HE rate constants, $k_{„}$, of the various radicals. At room temperature these are $k^{\wedge} = (1.7\pm0.2)10^5\ s^{-1}$. $k^{\wedge} = (7.5\pm1.0)1.0^8\ s^{\wedge}mol^{-1}$ and $k_{BB} = (1.0\pm0.2)1.0^8 s^{-1}moH$. The results also provide information on the longitudinal relaxation rates of both radicals which was found to depend on the radical concentration. The present work demonstrates the power of the 2D exchange EPR method in elucidating mechanisms of dynamic processes and determining kinetic parameters, in particular when several such processes occur simultaneously

139 ELECTRON SPIN RESONANCE STUDIES OF THE PHOTOOXIDATION OF PHENOTHIAZINE DERIVATIVES IN SILICAS OF DIFFERENT PORE SIZES. Bosong Xiang and Larry Kevan, University of Houston, Department of Chemistry, Houston, Texas 77204-5641.

Methylphenothiazine and other N-aikylphenothiazines were introduced into silica gel pores by impregnation and sol-gel synthesis. The alkylphenothiazines were photooxidized at room temperature by 320 nm irradiation to form stable alkylphenothiazine cation radicals detected by electron spin resonance and diffuse reflectance spectroscopies. The silica gel framework is suggested to be the electron acceptor. The photoyield and stability of the methylphenothiazine cation radical depend on the silica gel pore size,, In a small pore silica gel the methylphenothiazine cation radical has a larger photoyield and is more stable with a longer lifetime than in a large pore silica gel. Increasing the alkyl chain length up to hexadecyl does not affect the alkylphenothiazine cation photoyield or stability. However, addition of a anionic sulfate group to the alkyl chain of an alkylphenothiazine doubles its photoyield and increases the stability of the photoproduced radical, It is suggested that the mobility of the alkylphenothiazine cation radical in the silica gel pores controls its photoyield and stability.

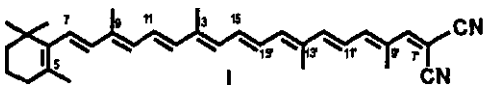
140 AN ENDOR STUDY OF SYNTHETIC CAROTENOID CATION RADICALS. A. S. Jeevarajan[3], L. Piekara-Sady[a], M. Plato[0] and Lowell D. Kispert[0]. a) Department of Chemistry, The University of Alabama, Tuscaloosa, AL-35487. b) Institut fur Molekulphysik, Freie Universitat Berlin, Arnimallee, Germany.

The importance of carotenoids in photosynthesis as a photoprotector and an auxiliary antenna pigment is well established. However, the role of the carotenoid cation radical in the photosynthetic apparatus is not well understood. Further, in order to incorporate the photoprotect character of the carotenoids in artificial solar devices, the decomposition processes should be understood. As part of this research effort, the cation radicals of *7,7'* dicyano-7'-apo-fi-carotene(I) and 7'-phenyl-7'-apo-fi-carotene (II) were generated photochemically in a silica gel matrix and their powder ENDOR spectra determined. RHF-INDO/SP semiempirical molecular orbital calculations were carried out on the AMI optimized geometries of the cation radicals of I and II. The following hyperfine coupling constants of nearly isotropic methyl protons were determined from the experimental ENDOR spectra.

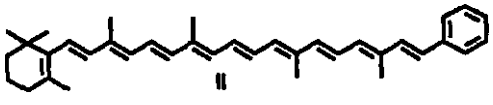
I C(5), C(9')-CH_3 : 4.3 MHz; C(13)-CH_3 : 6.9 MHz; C(9)-CH_3 :11.4 MHz and C(13')-CH_3 :15.7 MHz

II C(5)-CH_3 : 4.3 MHz; C(9')-CH_3 : 7.2 MHz; C(9)-CH_3 : 9.6 MHz; C(13)-CH_3 :13.5 MHz and C(13')-CH_3 : 14.0 MHz

It was found that the unpaired electron density increases as a function of electron accepting property of the substituent (I > II). This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy, under grant DE-FG-05-86ER13465.



I



II

EPR STUDY OF Fe DOPED AND H+ IMPLANTED INDIUM PHOSPHIDE. **W. Kevin**
141 **Kuhn and Margaret H. Rakowsky, The Frank J. Seiler Research Laboratory, 2354 Vandenberg 577suite 2A35, USAF Academy, CO 80840-6272 .**

Indium phosphide (InP) is a direct bandgap semiconductor used as a. semi-insulating substrate electronic devices. A thorough understanding of the dopants and defects in the InP substrate is ^°r°p ortant part of efforts to improve the quality of the substrate. In this study, we have examined the PPR spectra of InP that was iron doped and proton implanted (2 MeV, 1 x 10^{17} cm^{-3}). In addition to usual features between 2700 and 4000 Gauss, additional features have been observed. We have examined the angular and temperature dependence of the paramagnetic features concurrently and will discuss the observed dependence in terms of site symmetry and orientation.

142 **FOUR-PULSE ELECTRON SPIN ECHO ENVELOPE MODULATION STUDIES OF Ni(III)(CN)4(H_20)2-.** **Hnng-In Lee and John McCracken, Department of Chemistry, Michigan State University, East Lansing, MI 48823**

Four-pulse electron spin echo envelope modulation (ESEEM) studies aimed at characterizing the hyperfine interactions between protons of axially bound water molecules and nickel ion in Ni(IIF)(CN)4(H20)2" were carried out. The sum combination bands were chosen to be analyzed because the hyperfine interaction of the proton is strongly anisotropic. To analyze the ESEEM data, theoretical line shape singularities of the sum combination bands f ($v_.$+vp)/2J were determined as a function of ⊕; the azimuthal angle of the external magnetic field direction with respect to g-tensor. The frequency shifts of the singularity points of the sum frequencies from Larmor frequency [(Vcc+vp)/2-vi] were calculated as a function of magnetic field strength across EPR absorption spectrum to build a field profile. The field profile patterns were mostly determined by $6_„$, the angle between the principal hyperfine axis and g3 axis. The frequency shifts were sensitive to the electron-nuclear dipole-dipole distance. The isotropic hyperfine coupling had little affect on the profile patterns and the frequency shifts. The ESEEM data showed that the peak positions of the sum combination bands of the axial water proton in Ni(lH)(CN)4(H20)2~ were placed on one of the singularity points depending on t, the time interval between first and second pulses. The simulations for the field profile of the sum frequencies of the water protons gave the effective Ni-H dipole-dipole distance of 2.33±0.03 A, and the angle of 18±3° between the principal hyperfine axis and g3 axis. The isotropic hyperfine coupling constant of 2.5+0.5 MHz could be obtained by analysis of the T suppression behavior of four-pulse ESEEM experiments at a fixed field strength.

143 **EPR STUDY OF THREE E' VARIANTS IN MICROELECTRONIC QUALITY THIN FILM THERMAL $Si0_2$ ON Si.** **John F. Conlev. Jr. and Patrick M. Lenahan. Penn State University, University Park, PA 16802-1401, Howard L. Evans and Robert K. Lowry, Harris Semiconductor, Melbourne, FL, 32901, Thomas J. Morthorst, Harris Semiconductor, Findaly, OH.**

Thin film thermal Si02 films on Si are used as gate oxides in metal-oxide-semiconductor field effect transistors (MOSFETs), the devices that dominate modem microelectronics. The reliability of MOSFET devices is adversely affected by gate oxide charge trapping. Charge trapping in these oxides can result from hot carrier injection, increasingly a problem as device dimensions continus to shrink. Our recent investigation of a variety of thermal oxides during a study of microelectronic fab line problems has led to the observation of several spectra which we suspect are E' variants. (E centers are associated with unpaired electrons on oxygen deficient silicons.) Until recently, only one type of E' spectra had been reported in thin film amorphous $Si0_2$. This spectra is now referred to as E'y, after its designation in bulk fused silica by Griscom et al.. We present evidence that the three presumed E' variants, the E'g center, the EP (Provisional E' 1) center, and the EP2 (Provisional E' 2) center, have different generation mechanisms and different charge trapping properties. We confirm that the Eg center will dominate charge trapping under most circumstances and demonstrate that the EP1 center will probably contribute during low; very pure hole injection fluences. Most importantly, we observe a new defect, the EP2, not previously been reported in thin film SiO^. We present evidence that the EP2 is an impurity related E variant.

144 ENDOR AND ESEEM STUDIES OF Mn^{n}ADP COMPLEXES IN MYOSIN. **Jeanne Digell, Russell LoBruttot, Ivan Rayment*, Robert Smith*, L. Timothy Laughlin*, and George Fl! Reedt flDept. of Physics, Northeastern University, Boston, MA 02115; tDept of Botany, Arizona Stat University, Tempe, AZ 85287-1601; and ^Institute for Enzyme Research, University of Wisconsin Madison, 1710 University Avenue, Madison, WI53705.**

The structures of Mn^{n}ADP complexes with the SI fragment of myosin have been examined bv ENDOR and ESEEM at X-band. We have resolved both parallel and perpendicular components of the superhyperfine coupling from ^{31}P of the unliganded a-phosphate of ADP, in complexes with BeF_n- and with VO4- as y-phosphate analogs. From the ENDOR spectra, we have calculated the metal-^{31}P distance in each complex. ENDOR resonances were also observed from the P-phosphate in each complex. Three distinct, nonexchangeable *H ENDOR resonances were observed which most likely arise from one or more protein-based ligands. The effect of high spin multiplicity (S=5/2) on these spectra will be discussed. ESEEM measurements on the complex with BeF_n~ reveal an intense modulation which is attributed to ^{9}Be. The observation of this resonance, in combination with a strong (probably ^{19}F) doublet splitting observed in the 35 GHz CW spectrum, suggests that BeF_n- also coordinates Mn^{11}. This result has implications for the sequence of chemical events in the muscle contraction cycle.

145 SPIN COUPLING IN DINITROXYL DERIVATIVES OF DIAZA-CROWN ETHERS: EFFECT OF BIVALENT IONS BINDING. **Irina I. Lobysheva. Anatoly B. Shapiro and Michael G. Goldfeld, Institute of Chemical Physics, Russ. Acad. Sci., 4, Kosygin st., Moscow 117977, Russia.**

We describe novel dinitroxyl derivatives of diaza-18-crown-6 and diaza-15-crown-5. Binding of bivalent ion to .crown core exerts influence on spin exchange coupling between free-radical moieties. Complexation results in the appearance of two additional components in the ESR spectum due to decrease of mean distances separating both unpaired electrons. The effectivity of cation binding strongly dependends on their respective ionic radii. This phenomenon permits to titrate bivalent ions in solution and in some cell compartments, or liposomes.

146 TEMPERATURE DEPENDENT PULSED EPR RELAXATION STUDIES OF THE S_2 STATE MULTILINE SIGNAL OF THE PHOTOSYNTHETIC OXYGEN EVOLVING COMPLEX. **Gary A. Lorigan and R. David Britt, Department of Chemistry, University of California at Davis, Davis, CA 95616, (916)-752-7703.**

The electron spin-lattice relaxation rate (1/Xi) of the *g=2* "multiline" signal arising from the photosynthetic oxygen evolving complex of Photosystem II poised in the *S2* state has been directly measured over the temperature range of 4.2 K to 11 K, via the inversion-recovery pulsed EPR technique. The electron spin echo amplitude of the *g=2* "multiline" signal varies inversely with temperature indicating ground spin state Curie law behavior, agreeing with our previously reported work. A natural log plot of the electron spin-lattice relaxation rate versus reciprocal temperature is consistent with an Orbach mechanism as the dominant relaxation pathway for the "multiline" signal. This relaxation behavior indicates that an excited spin state exists 36.5 cm^{-1} above the ground state "multiline" signal.

- **LOCAL REARRANGEMENT OF A CRYSTAL LATTICE NEAR IMPURITY IONS AND ITS INFLUENCE ON MAGNETIC PROPERTIES OF CRYSTALS, L.K. Arninov, Kazan State University, Kazan, Tatarstan-Russia 420008**

Real crystals contain different impurity centers; moreover they are often activated by magnetic impurities either with the purpose of imparting necessary properties to material or ^ robes for investigation of crystal characteristics. In diamagnetic crystals paramagnetic ^s unties are the only source of magnetism. On the other hand, if a matrix crystal is a kind of magnetic its magnetic properties may be noticeably changed by implantation of alien atoms. This is due mainly to the rearrangement of a crystal lattice in the neighbourhood of impurity centers, the corresponding change of a crystal field and energy spectra of matrix ions. We are considering these problems, paying special attention to Van Vleck paramagnets - crystals of lanthanide compounds activated by other lanthanide ions. Paramagnetic susceptibilities, NMR characteristics are calculated, the reverse effect of the lattice rearrangement on EPR characteristics of paramagnetic impurities itself is considered in detail.

408 AN INDUSTRIAL APPLICATION OF EPR: NEARLY CONTINUOUS STUDY OF PROPAGATING RADICALS IN BATCH EMULSION POLYMERIZATION OF MMA. Hsiu-Rong Chang, Hsing-Yeh Parker§ and David G. Westmoreland, Rohm and Haas Company, 727 Norristown Road, P.O. Box 904, Spring House, PA 19477-0904. § Rohm and Haas Company, Rt.13 and 413, Bristol, PA, 19007.

A specially designed experimental system has been developed at Rohm and Haas Company which combines electron paramagnetic resonance (EPR) and a continuous flow system to study the batch emulsion polymerization of methyl methacrylate (MMA). A gravity flow stream and a time-sweep data acquisition technique allows essentially continuous monitoring of the propagating free radical concentration during the entire reaction. The experimental setup and examples of studies carried out with it will be presented.

409 ANOMALIES IN FLUORINE AND NITROGEN HYPERFINE SPLITTING CONSTANTS OF NITROXIDES IN VARIOUS SOLVENTS. Jane Z. Chen. Yong-Kang Zhang, Uwe M. Oehler, Edward G. Janzen, Oklahoma Medical Research Foundation, National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, 825 NE 13th St., Oklahoma City, OK 73104, USA. University of Guelph, MRI Facility, Ontario Veterinary College, Guelph, Ontario, Canada NIG 2W1.

I has been believed since the beginning of time that the nitrogen hyperfine splitting constants (N-hfsc's) of nitroxides increase with increase in solvent polarity. This is because the nitroxyl function has a polar contribution from a dipolar resonance structure. This contribution is enhanced in polar solvents. Hydrogen-bonding protic solvents provide an additional polar enhancement which leads to large N-hfsc's for nitroxides in water. This work however provides an example of nitroxide which does not fit this generalization. The N- s of trifluoromethyl alkyl and aryl nitroxides show almost no polar solvent effect. Thus, trifluoromethyl 'w-outyl nitroxide has almost the same N-hfsc in solvents varying in polarity from THF to methanol. It is a so known that *(3-H* hfsc's increase in magnitude in alkyl or alicyclic nitroxides as the solvent polarity increases. This is direct evidence that the spin density increases on the nitrogen atom of the nitroxide as the *V* °f.tliesolvent increases. However, in trifluoromethyl alkyl nitroxides the |8-F hfsc actually decreases e try with increase in solvent polarity! These results will be shown and some possible mechanisms suggested. r J-

410 **MULTIFREQUENCY ENDOR OF A NITROXIDE.**

T. Christidis and James S. Hyde ,
Physics Department, American University of Beirut, 8^50 Third Ave., New York, NY 10022
Biophysics Institute, Medical College of Wisconsin, Milwaukee, WI 53226

ENDOR has been generally periormea at X band or higher. For nuclei with large hyperfine interactions and small gyromagnetic ratios there is a large enhancement of the rf field that is inversely proportional to the operating microwave frequency. For nitrogen nuclei in nitroxides, the enhancement is about 20, 60 and 180 at X, S and L bands respectively.

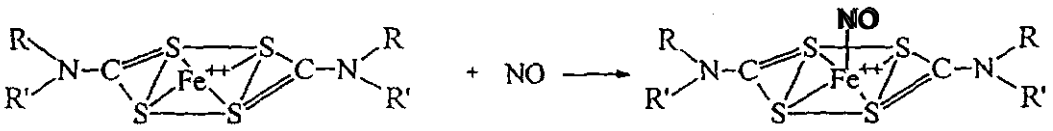
We have performed ENDOR of TEMPONE in n-heptane at microwave frequencies ranging from 9.6 to .1.1 GHz. The ENDOR probehead employs loop-gap resonators surrounded by the rf coil. Effective rf fields of up to 160 mT in the rotating frame were obtained. At L band, the static second order effects that are larger than the nuclear Zeeman interaction can accurately account for the positions of the ENDOR lines. The ENDOR enhancement is found to saturate at 17% for "N at L band. The ratios of the intensities of the ENDOR lines are found to be independent of the microwave frequency. Similar coherence effects of both the microwave and rf fields are observed for both ^{15}N and ^{n}N

411 **A MULTIFREQUENCY ENDOR STUDY OF FLUORIDE BINDING OF HEMOPROTELNS, Yang C. Fann. Judith M. Nocek, Jui-lin Ong, and Brian M. Hoffman, Department of Chemistry, Northwestern University, Evanston, IL 60208-3113.**

Frozen solutions of fluoromet-hemoproteins, for example, hemoglobin, myoglobin, horseradish peroxidase, cytochrome c peroxidase, etc. were studied by pulse and continuous-wave electron nuclear double resonance (ENDOR) techniques. Fluoride is bound as the sixth ligand to the heme and the EPR spectra of hemoproteins exhibit high spin signals (gj = 2,g^ = 6) with resolved ^F superhyperfme splitting in the g=2 region. The ^F ENDOR signals were monitored through the EPR envelope and their hyperfine tensors were obtained by simulating field-dependent ENDOR spectra. The fits demonstrate that the fluoride is tilted slightly (3-5°) off the principle g-axis. An exchangeable proton with a coupling constant about 3-4 MHz was found in all cases. This proton is assigned as hydrogen bonded to the fluoride ligand and is essential for fluoride binding. Work on mutations of the distal heme pocket will also be discussed.

412 **CHARACTERIZATION OF IRON(II) DITHIOCARBAMATES AS NITRIC OXIDE SPIN TRAPS. Yashige Kotake, Torn Tanigawa, Mari Tanigawa, Ikuko Ueno and Edward G. Janzen, National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, Oklahoma City, Oklahoma 73104 U. S. A.**

Iron (II) complex of N-substituted dithiocarbamate in solution have been used in spin trapping of nitric oxide produced in biological systems such as in the septic mouse model and activated macrophages.



Hyperfine structure of the EPR spectrum of the spin adduct provides direct evidence for the presence of nitric oxide. Stability of spin traps and the resulting spin adduct is influenced by various factors such as oxygen concentration and the kind of buffer used. Water solubility of both dithiocarbamate and its iron (II) complex depends on the kind of functional group attached to nitrogen in dithiocarbamate. We have evaluated spin trapping capabilities of iron (II) complexes of several N-substituted dithiocarbamates using well defined nitric oxide source.

147 ELECTRON SPIN RESONANCE INVESTIGATIONS OF FREE RADICAL TOXICOLOGY. Ronald P. Mason. Nail. Institute of Environmental Health Sciences, NIH, Research Triangle Park, NC 27709; (919) 541-3910.

Since a large number of xenobiotics are metabolized to free radicals, an overall view of this area is not obvious. By definition, free radical metabolites must exist free of the enzyme, and, therefore, enzyme-xenobiotic transition states with free radical character such as are thought to exist in the cytochrome P-450 substrate complex are excluded. It follows that if the rate of formation of the free radical is fast enough, it can be detected with ESR and will have the same ESR spectrum as the free radical made by purely chemical means. Many free radical metabolites of drugs and toxic chemicals can be detected *IN VITRO* at steady-state concentrations, although the fast-flow or spin trapping techniques are sometimes necessary. *IN VIVO* detection is possible through the spin trapping technique, and *IN VIVO* spectroscopy may yet be possible. Most of the free radical metabolites formed by one-electron oxidation are formed by peroxidases (e.g., myeloperoxidase, lactoperoxidase, etc.). Both the classic heptotoxicant carbon tetrachloride and the classic pulmonary toxicant paraquat are toxic because they are enzymatically reduced to free radicals. The dose-limiting cardiotoxicity of the anti-cancer agent adriamycin is also thought to be due to free radical formation. In summary, ESR can be used to screen compounds for potential toxicity *VIA* a free radical metabolism. Although no approach can be expected to predict toxicity, and false negatives are likely because free radicals are so reactive, no false positives are known where a free radical metabolite has been detected *IN VIVO*.

148 **TWENTY-FIVE YEARS OF SPIN TRAPPING. Edward G. Janzen. National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, Oklahoma City, Oklahoma, and Departments of Clinical Studies and Biomedical Sciences, MRI Facility, Ontario Veterinary College, University of Guelph, Guelph, Ontario.**

On the 50th anniversary year of EPR spectroscopy this presentation will begin with early applications of EPR to physical organic chemistry in general and spin trapping (ST) in particular. The ST approach was originally designed for in situ chemical systems with particular emphasis on the analytical aspects of the experiment, i.e. detection of and structural assignment to the reactive free radicals in the solution of interest. Nitrones and nitroso compounds served this purpose well; each type demonstrating advantages and disadvantage depending on the reaction under investigation. When biological applications were shown to be feasible the problem became more complex. Since truly in vivo in situ experiments in useful animal models are not feasible at X-band EPR, the ST products must be removed from the animal and isolated for analysis. Although some successful studies are well known, many other attempts have been disappointing. It is clear that improvements in ST methodology are necessary and some ideas along these lines will be presented.

149

Abstract Not Available

150 STRUCTURE AND DYNAMICS OF MEMBRANE PROTEINS.

Christian Altenbach and Wayne L. Hubbell, Jules Stein Eye Institute, University of California Los Angeles, 100 Stein Plaza, Los Angeles, CA, 90024-7008, ®310-206-8831.

Site-directed spin labeling (SDSL) of membrane proteins allows the attachment of nitroxide spin labels at any desired position in the protein sequence. The accessibility of the nitroxide side chains to collision with dissolved paramagnetic reagents reveals the topography of the sites, while analysis of the EPR spectral lineshapes provides information on the side chain dynamics. The introduction of two spin labels permits the determination of the distance between selected sites from the dipole-dipole interaction in the solid state. With a sufficiently large set of mutants, this data can be analyzed in terms of the protein secondary and tertiary organization at the level of the backbone fold. In addition, changes in protein structure at this level can be followed with millisecond time resolution. Thus SDSL is ideally suited to study "rigid body" movements of secondary structure during protein function as well as protein folding.

151 ***IN VIVO*** **IMAGING WITH VERY LOW FREQUENCY EPR: PROGRESS AND IMPLICATIONS FOR FUTURE MEASUREMENTS.** H.J. Halpern[1]. C. Yu\ E.D. Barth[1], M. Peric[1], W.E. Boisvert[1], S. Kasa[1], M.W. Makinen[1], S. Pou[2] and G.M. Rosen[2], University of Chicago, 5841 S. Maryland Ave., Chicago, IL. 60637 and University of Maryland, 20 N. Pine St., MD 21201

Spectral-spatial imaging of spin label signal within a living sample provides crucial information unavailable without the localization capacity. Spectral spatial imaging has been applied to EPR oxymetry to simultaneously extract line widths and separations from different volumes of murine tumors. The use of partially deuterated spin label probes allows both improved spatial resolution and signal intensity. Particulate probes with very narrow lines also allows high resolution. Resolution of both spectral and spatial parameters is dependent on sample size and linewidths as well as signal intensity. The effect of animal motion on these parameters is also non trivial. Measurements are presented at 250 MHz, a frequency low enough for good penetration and low dispersion in tissue samples of 5-7 cm in a containment resonator. It is hoped that the first measurements with three spatial dimension distinction using stepped gradients will be available. Examples from low frequency spin trapping and organ specific pharmacodynamics will also be discussed. (CA50679, Ale. Bev. Med. Res. Fdn., Co. Tob. Res., DCB-8616115, HL33550)

152 **MELANIN AND NEUROMELANIN—A BIOPHYSICAL PERSPECTIVE.** Tadeusz Sarna. Institute of Molecular Biology, Jagiellonian University, 31-120 Krakow, Poland

Melanins occur in humans in melunocytesin skin, in neuroepithelial cells of the retina, iris and ciliary body of the eye; in the inner ear; and in the vicinity of certain dopaminergic neurons of the midbrain. It is an amorphous, polymeric materials with physicochemical properties that include: electron- and ion-exchange capabilities, photoreactivity, antioxidant activity, paramagnetism, and resistance to classical analytic chemical techniques. The exact biological role of melanins, remains unclear. EPR has proven to be one of the most effective means to study these otherwise intractable molecules, especially with recent advances in EPR technology, especially high frequency EPR and exploitation of the effects of pH. This approach is especially promising in the study of neuromelanin, a naturally occurring pigment which may be altered in degenerative diseases such as Parkinson's disease. We have studied natural neuromelanin and synthetic polymers obtained from oxidative polymerization of dopa and dopamine and their co-polymerization with cysteine or glutathione. Using X- and W-band EPR, in conjunction with other analytical techniques in the study of natural and model melanins, in regard to their structure and the antioxidant efficiency of native melanin polymers and the effect of oxidative bleaching, have led to promising models for the structure of human neuromelanin. Based on melanin's ability to sequester redox-active metal ions, a hypothesis on the biological role of neuromelanin and retinal pigment melanin has been developed.

153 **IN VIVO EPR SPECTROSCOPY: PROGRESS AND POTENTIAL FURTHER DEVELOPMENTS.** Harold M. Swartz. Dartmouth Medical School, Hanover, N.H., 03755

The capability of EPR to study processes in vivo by the use of EPR spectroscopy has proven to be an unexpectedly productive approach which already has led to biologically important progress and which has the potential for widespread applications in experimental and, perhaps, clinical studies. The progress has occurred because of a combination of instrumental developments (especially low frequency EPR spectrometers, loop gap resonators, coupled circuits, and methods to compensate for physiological movements), paramagnetic probe developments (synthesis of nitroxides and identification of new oxygen sensitive materials) and conceptual insights as to biological problems for which in vivo EPR spectroscopy can provide Valuable data. The spectroscopic approach is complimentary to imaging, providing the full power of spectroscopy but only limited spatial information. While there appear to be a number of very promising applications of this technique, the most productive approach so far has been to measure p02 in tissues and the success of these studies alone seems to assure an important role for this technique for many years. The presentation will highlight the key developments that have occurred, the most recent results obtained with this approach, and the possible direction of future developments.

154 OXIMETRY STUDIES USING 3D/4D SPECTRAL-SPATIAL EPR IMAGING OF BIOLOGICAL ORGANS AND TISSUES AT L-BAND. Periannan Kuppusamy, Michael Chzhan and Jay L. Zweier, The EPR Laboratories, The Johns Hopkins Medical Institutions, 5501 Hopkins Bayview Circle, Baltimore, Maryland 21224.

In order to study the spatially defined differences in free radical metabolism and oxygenation in biological organs such as the heart, electron paramagnetic resonance imaging (EPRI) instrumentation enabling the performance of 3D/4D spectral-spatial images of free radicals has been developed Procedures for selecting optimized parameters for projection acquisition, instrumentation and algorithms for correcting drifts in microwave frequency and inaccuracies in the static and gradient magnetic fields were developed and used. Using this instrumentation 3D/4D spectral-spatial as well as 3D spatial images of isolated perfused rat hearts were obtained. In the isolated rat heart, imaging experiments were performed to determine the kinetics of radical clearance at different spatial locations within the heart, during myocardial ischemia. The kinetic data showed the existence of regional and transmural differences in myocardial free radical clearance. It was further demonstrated that EPRI could be used to non-invasively measure spatially localized oxygen concentrations in the heart.

155 SELECTIVE HOLE BURNING AND ITS APPLICATION TO PHOTOSYNTHESIS

Asako Kawamori, Yoshio Kodera and Sergei A.Dzuba*.
Faculty of Science, Kwansei Gakuin University, Nishinomiya 662, Japan,
institute of Chemical Kinetics and Combustion, Russian Academy of Sciences, 630090 Novosibirsk, Russia

A novel electron spin echo method has been established to detect the spectral diffusion caused by dipole interaction between the paramagnetic species. This method is based On the selective hole burning and the subsequent detection of the hole broadening using FID and echo shape. The hole broadening is determined by the local magnetic field fluctuations at the site of the monitored spin, caused by random flips of other spins situated nearby.

The simple theory was presented with an example of pairwise distribution of radicals in coal [1]. Then, this method is applied to study dipole interactions of tyrosine Y_D^+ radical with the manganese cluster in oxygen-evolving center and with Fe^{2+} ion on the acceptor side of Photosystem II (PS II). In the manganese-depleted PS II, the distance from Y_D^+ to Fe^{2+} ion has been determined to be less than 52 A. The distance from Y_D^+ to the manganese cluster was estimated to be 28 A in the S2 state and 30 A in the Sj state. The distribution of the distance was estimated to be in the range 4 - 6 A.

[1] Dzuba, S. A., Kodera, Y., Hara, H. and Kawamori, A. (1993) J. Magn. Res. A 102, 257-260

156 EPR AND ENDOR STUDIES OF THE ELECTRONIC STRUCTURE OF PIGMENT RADICAL IONS IN NATIVE AND GENETICALLY MODIFIED BACTERIAL REACTION CENTERS.

F. Lendzian[1], J. Rautter[1], H. KaB[1], F. Muh[1], M. Kuhn[1], J.P. Allen[2] and W. Lubitz[1]. [1]Max-Volmer-Institut fur Biophysikalische und Physikalische Chemie, Technische Universitat Berlin, D-10623 Berlin, Germany; [2]Chem. Dept., Arizona State University, Tempe AZ 85287-1604, USA

The spatial structure of the bacterial photosynthetic reaction center (RC) has been determined by X-ray diffraction for two purple bacteria species. Since then many recent investigations have concentrated on the relationship between the spatial and electronic structure of RC components and their functional properties. Structural changes can be introduced by chemical modifications or by site-directed mutagenesis. Here, we report on the investigation of the electronic structure of cation and anion radical states of components of the light-driven electron transfer (ET) chain using 'hyperfine spectroscopy" (cw and pulsed EPR and ENDOR). For the cation radical of the primary donor and the anion radical of the intermediate acceptor in *Rb. sphaeroides* it is shown that (i) specific H-bonds to protein residues can be identified and geometrically characterized (O ... H distance) and (ii) the influence of such H-bonds on the orbital symmetry and orbital energies can be determined. The results reveal a delicate balance of spin densities between the two bacteriochlorophylls constituting the primary donor that is strongly influenced by the presence or absence of specific H-bonds to amino acid residues of the surrounding. This may be of functional importance for the efficient unidirectional ET. The results demonstrate the potential of EPR techniques for the investigation of the structure-function relationship in photosynthetic RC's.

157 2_H ELECTRON SPIN ECHO ENVELOPE MODULATION STUDIES OF STRONG a-HYDROGEN HYPERFINE COUPLING IN ORGANIC RADICALS **Kurt Warncke and John McCracken. Department of Chemistry, Michigan State University, East Lansing, MI 48824**

Electron Spin Echo Envelope Modulation (ESEEM) spectroscopic methods have been used to measure the complete ^{2}H hyperfine coupling tensors for the a-3,5-deuterons of a tyrosine neutral radical model system and for the a-3,5- and P-CH2- deuterons of one of the redox active tyrosine residues of the Photosystem II electron transport system from *Synechocystis* 6803. Stimulated-echo (90°-T-90°-T-90°) ESEEM data were collected using the microwave pulse-swapping sequence described by Fauth, etal. (J. Magn. Reson. 66, 74-86 (1986)). Division of the envelope modulation data from ^{2}H-substituted radical samples by that from per-protonated radical samples was used to remedy discontinuities in background decay and amplitude introduced in the envelope by the eclipse of the second and third microwave pulses. For a-3,5-^{2}H tyrosine radicals, ESEEM data were collected using *x* values that ranged from 214 to 1295 ns and a common instrument dead time of 140 ns. Spectra collected at 9.1 GHz and 0.3265T, show broad fundamental, Ami = ±1. peaks with frequency components ranging from 0.4-1.6 and 3.3-4.5 MHz, and a broad double quantum feature that covers a spectral extent from 6.8-8.0 MHz. The results show that sculpting of the ESEEM lineshapes by the suppression effect allows retrieval of information, obscured by the orientation dependence of the modulation depth, that is necessary to determine the rhombic hyperfine tensor.

158 THE MECHANISM OF HYDROLYSIS OF p-LACTAM ANTIBIOTICS: STRUCTURES OF A SPIN-LABELED PENICILLIN AND ITS HYDROLYTIC REACTION INTERMEDIATES DETERMINED BY ENDOR. **D. Mustafi and M. W. Makinen, The University of Chicago, Chicago, IL 60637.**

We have synmesizedA^-(3-formyl-2,2,5,5-tetramemyl-l-oxypyrrolmyl)-peniciu as a specific substrate probe of p-lactamase. With p-lactamase I of *B. cereus,* the steady state kinetic parameters kcat of 1800 s-l and *KM* of 100 uM at 22 °C and pH 7 show that this paramagnetic substrate probe is as kinetically specific and catalytically reactive as benzylpenicillin. The conformation of the spin-labeled penicillin free in solution has been determined by ENDOR and molecular modeling. From analysis of ENDOR spectra the principal hfc components of specific protons in the fused p-lactam ring were determined. The dipolar hfc components yielded electron-proton separations between the unpaired electron on the nitroxyl group and corresponding assigned protons. The conformation of the spin-labeled penicillin was determined on the basis of torsion angle search calculations constrained by ENDOR-determined distances. The ENDOR-determined conformation of the spin-labeled penicillin is almost identical to that of the X-ray defined structure of amoxycillin. We have also determined by ENDOR the location of a solvent molecule that is hydrogen-bonded to the penicillin in a position near the lactam group. For the free spin-labeled penicillin in solution, the hydroxyl group of this solvent molecule is positioned on the "endo" side of the p-lactam ring, as if it were poised for nucleophilic attack on the carbonyl carbon of the p-lactam. This observation is important because "endo" attack of a fused p-lactam compared to "exo" attack is hindered sterically but favored stereoelectronically. The importance of these results with respect to the mechanism of hydrolysis of p-lactams will be discussed. (Supported by GM 21900).

159 EPR METROLOGY AT THE NIST. **Marc F. Desrosiers. Debra L. Bensen, James M. Puhl, Ionizing Radiation Division, Building 245 / Room C229, National Institute of Standards and Technology, Gaithersburg, Maryland 20899**

More than three decades ago, it was discovered that stable free radicals are formed in gamma-irradiated crystalline alanine, an amino acid. It was intended that alanine be used in radiation dosimetry. However, the size, expense and complexity of the EPR instrumentation precluded their practical entry into the dosimetry laboratory. Faced with increased demands to provide more reliable and precise assurances of absorbed dose, the radiation processing industry is considering the alanine-EPR system to address their needs. This renewed interest in alanine-EPR dosimetry has driven the development of compact low-cost spectrometer and prompted commercial dosimeter manufacturers to consider mass production of alanine dosimeters for the radiation sterilization industry. The current status of alanine dosimetry will be discussed, along with research into new materials. The broadest range of radiation measurement applications for a single material is found for bone. Radiation damage in bone has been used in: irradiated food detection; radiation accident dosimetry; medical therapy with internally-administered bone-seeking radionuclides; archeological dating. Furthermore, recent improvements in EPR imaging and microscopy may also provide absorbed-dose profiles in unprecedented detail.

160 HIGH FREQUENCY DYNAMIC NUCLEAR POLARIZATION and ELECTRON PARAMAGNETIC RESONANCE **L. R. Becerra[a], G. Gerfen[a], J. Bryant[a], B. F. Bellew", D. Hall", S. Inati«, K. J. Kreischer[c], R. J. Ternkin* D. J. Singel[c] and R. G. Griffina** [a]*Frands Bitter National Magnet Laboratory , Department of Chemistry,* [b]*Plamsa Fusion Center, MIT,Cambridge, MA 02139* [c]*Department of Chemistry, Harvard University, Cambridge, MA 02138*

Signal-to-noise (S/N) in high resolution solid state NMR experiments can be enhanced with dynamic nuclear polarization (DNP) techniques involving irradiation of the EPR spectrum of paramagnetic samples with microwaves. DNP has been performed successfully at frequencies < 40 GHz for e~'s (60 MHz for *H),* and in favorable cases enhancements range from -20-250. However, because of the absence of high power microwave sources operating at > 40 GHz, these experiments have not been executed at the higher fields commonly employed to enhance sensitivity and resolution in NMR experiments. Recently, we have developed the necessary instrumentation to extend DNP experiments to higher frequencies. First, we have assembled a 140 GHz pulsed and CW EPR spectrometer, since it is important to know the shape of the EPR spectrum as well as the relaxation times of the associated paramagnetic center. Second, we have constructed a CW gyrotron - a high frequency, high power microwave oscillator - operating at 140 GHz (210 MHz for !H) and incorporated it into a DNP/NMR spectrometer. The design and operation of this device in pulsed and CW mode will be discussed, results illustrating DNP enhanced NMR spectra will be presented, and the possible extension of these techniques to higher operating frequencies will also be considered.

161 PULSED ENDOR SPECTROSCOPY OF ^{57}Fe CONTAINING ZEOLITES. P. Goldfarb*. M. Bernardo, K.G. Strohmaier and D.E.W. Vaughan, Exxon Research and Engineering Co.; Route 22 East, Clinton Township; Annandale, NJ **08801**

The catalytic properties of zeolites can be modified by variations of the zeolite composition such as the incorporation of Fe^{3+} into tetrahedral (T) framework sites. The EPR spectra of such materials usually reveal several types of Fe^{3+} signals indicating the coexistence of both framework and non framework iron. The assignment of the signals is, however, most often ambiguous. In order to obtain a better characterization of the Fe^{3+} sites pulsed electron-nuclear double resonance (ENDOR) experiments on ^{57}Fe enriched zeolites were carried out. The latter provides the NMR spectrum of the ^{57}Fe from which the hyperfine coupling is readily obtained. Moreover, the NMR spectrum can resolve Fe^{3+} sites with overlapping EPR signals. Pulsed ENDOR measurements were performed on ^{57}Fe-Sodalite which is unique in the sense that its EPR spectrum is characteristic of a single species assigned to framework T sites. Therefore it can serve as a reference for T sites in zeolites. The peaks observed were assigned using hyperfine selective ENDOR experiments and orientation selective experiments. The effect of the zero field splitting on the ENDOR spectra , the use of pulse ENDOR in the investigation of the synthesis mechanism of ^Fe-Sodalite and spectra obtained from other zeolites will be discussed as well.

"•"Permanent address: Chemical Physics Department, Weizmann Institute of Science, Rehovot 76100, Israel

162 **DYNAMIC NUCLEAR POLARIZATION OF SOLVENT NUCLEI IN SOLUTIONS CONTAINING FREE RADICALS.** **Richard D. Bates. Jr.. Department of Chemistry, Georgetown University, Washington, DC 20057.**

An overview of the contributions of dynamic nuclear polarization (DNP) to studies of interactions of solvent species and paramagnetic probes in solution will be presented. Measurements will be compared with studies of the same systems by other magnetic resonance methods. Low field DNP investigations of nuclei interacting in solution with free radicals have provided important information about electronic structure of the two species by identifying the relative contributions of scalar and dipolar coupling of the nuclear and unpaired electron spins. The paramagnetic-species induced component of the relaxation of solvent nuclei provides complementary information by acting as a sensitive probe of the molecular motions of the interacting nuclear and unpaired electron spin. Separation of the dipolar contribution arising from rotation of the transient complex from the translational diffusion of the species free in solution has been achieved by varying the solvent composition with an inert cosolvent. Current investigations of solvent-solute interactions between proton donors and nitroxide radicals examine the dynamics of short-lived complex formation on the molecular level by a range of magnetic resonance approaches.

163 **A. SELECTIVE OBSERVATION OF SILICA SURFACES BY ^{29}Si DYNAMIC NUCLEAR POLARIZATION/MAGIC ANGLE SPINNING NMR** **Jun.ji Kobayashi. Materials and Electronic Devices laboratory, Mitsubishi Electric Corp., Hyogo 662, JAPAN**

^{29}Si direct polarization spectra of the silica surface have been selectively observed via dynamic nuclear polarization (DNP) combined with magic angle spinning(MAS). The DNP enhancement of a nuclear polarization has not been reported so far on any surface species. We could observe the enhancement of at least a factor of 50 on ^{29}Si solid NMR spectra. The dehydrated silica surfaces were coveraged with approximately 0.5% monolayer BDPA free radicals. The electron polarization was transferred directly via DNP to the Si spin system. No enhancement has been obtained with the electron spin polarization transferring to the proton spin system. The samples above-mentioned were outgassed to 10"' Torr because the spin lattice relaxation rate of the unpaired electron of BDPA is needed to be as long as possible. The depth of enhanced regions of ^{29}Si polarization was deeper via the DNP transfer from the electron spin system than via the cross polarization transfer from 'H nuclear spin system. In addtion, the signals due to surface species such as (lip)Si (OSi)$_3$, (IK))$_2$Sr(OSi)$_?$ were more enhanced than that due to the bulk silicon (Si (OSi)$_4$). 1 woulcT like to thank Prof.Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-0002.

164 Advances in high-frequency, pulsed EPR/ENDOR spectroscopy

J. Schmidt
Huygens Laboratory, University of Leiden, The Netherlands

The main incentives to develop EPR spectroscopy at mm wavelength are the high spectral resolution, resulting from differences in or anisotropy of the g-factors of the various paramagnetic species, and the high absolute sensitivity that can be achieved. In this talk I will briefly review the main aspects of the 95 GHz, pulsed EPR spectrometer which has been constructed at the University of Leiden. Then I will illustrate its performance by presenting the results of three recent experiments.

The first example concerns a study of the photo-induced, shallow electron center in AgCL which is thought to be the precursor of the formation of the latent image. The high resolution that can be achieved is illustrated by the first observation of the complete ENDOR spectrum of this center involving the ^{107}Ag, ^{109}Ag, ^{35}Cl and ^{37}C1 nuclei. The high absolute sensitivity of the spectrometer is illustrated by the first observation of the EPR spectrum of the metastable triplet state of a minute single crystal of Qo (dimensions 0.2 x 0.2 x 0.2 mm^3). Further I will present the first EPR spectrum of a single crystal of the blue-copper protein azurin (dimensions 0.1 x 0.1 x 0.5 mm^3). Here it proved possible to determine the principal axes of the g-tensor of all 16 sites in the unit cell. Recently we even succeeded in observing the ^{14}N ENDOR spectra thus allowing for a determination of the electronic wavefunction.

165 "Solid State NMR, Pulsed ENDOR, and Multiple Quantum Spectroscopic Studies of Interfaces in Fullerene Polymer Blends", M. Afeworki, M. Bernardo, and H. Thomann. Exxon Corporate Research Lab, Rt 22 E, Annandale, NJ 08801

We have observed an increase in the thermally and mechanically measured glass transition temperature for elastomers solution blended with a few weight per cent fullerenes. In general, the modification of the viscoelastic properties of polymers is mediated through the interface between the dopant and polymer, particularly the molecular dynamics at the interface. We have taken advantage of two unique properties of the C60 molecule, its characteristic 13C resonance and its low reduction potential, to investigate the interface between the C60 molecule doped into polyisoprene and ethylene propylene copolymers using a variety of magentic resonance techniques. Results from variable temperature proton linewidth, 1H-13C cross polarization dynamics, selective cross polarization, pulsed EPR measurements of the C60 radical relaxation, EPR detected multiple quantum (MQ) NMR and MQ-ENDOR experiments will be presented.

166 **THE USE OF ENDOR TO IDENTIFY THE ATOMIC STRUCTURE OF DEFECTS IN DIAMOND-** **J.M. Baker and M.E. Newton, Oxford Physics, Clarendon Laboratory, Parks Road, Oxford, 0X1 3PU, U.K.**

Although nearly 100 paramagnetic defects have been catalogued in diamond by spin hamiltonian parameters measured by EPR, very few of these have been unambiguously associated with an atomic model. It has been necessary to use ENDOR to obtain enough information to make proper assignment of such models. The reasons for the limitation of EPR, and the way in which ENDOR overcomes these limitations, are discussed. Most ENDOR measurements have so far been of ^{14}N ENDOR made on substitutional nitrogen atoms, and a few have been made of ^{13}C ENDOR. The interpretation, as a source of information about molecular orbitals and structure in diamond, of hyperfine structure in terms of unpaired electrons, and of quadrupole interaction in terms of all electrons, is evaluated by reference to two well documented examples. The salient contribution from ENDOR for the assignment of a model is examined for each of the well characterised defects. The structure of the defects is not only interesting intrinsically, but also as a means of examining and understanding the processes of solid state chemistry which go on under appropriate conditions of temperature and pressure, or optical excitation. The possibilities are discussed for using ENDOR to increase the number of well characterised centres.

' **VERY-HIGH FREQUENCY EPR CALCULATION OF G- AND A-TENSORS; FROM HUCKEL THEORY TO AB INITIO.** **M.J. Nilees. R.L. Belford, W. Wang, and R.B. Clarkson. Illinois EPR Research Center, University of Illinois, 506 S. Mathews Urbana, II. 61801.**

Interest in and ability to perform calculations of g- and A- matrices of radicals has been in decline since magnetic resonance theories and MO-SCF theories were first developed some twenty to thirty years ago. While early Hiickel and semiempirical theories brought quick successes and popularity, the applications of more recent and more advanced semiempirical and *ab initio* MO theories have brought disappointingly small improvements and have seen little practical use. This has been in part because MO theories are designed primarily to calculate *orbital* energies and only secondarily to handle *spin* states. Here we examine the ability of various MO theories and configurational schemes to predict ground state spin-densities. With the development in EPR at frequencies of 100 GHz or greater, bringing very accurate experimental parameters, there is a new stimulus for such calculations, especially those of the g-matrix and its dependence on solvent interactions. This paper presents g-matrix calculations by several methods including excited state perturbation theory, finite perturbation theory, and configuration interaction/excited state perturbation theory as applied to various semiempirical MO and *ab initio* MO theories. Results are presented and compared for a number of free radicals. **Research supported by NIH grants RR01811 and GM42208.**

oo **HIGH SPIN IRON AT HIGH FREQUENCY: MULTIPLE TRANSITIONS AND PREDICTED EFFECTS OF PARAMETER DISTRIBUTIONS AT 9-250 GHz.** **K.S. Doctor, B.J. Gaffney and H.J. Silverstone, Department of Chemistry, Johns Hopkins University, 3400 N. Charles St., Baltimore, MD 21218**

In the last decade, the EPR spectra of a number of new heme- and non-heme proteins with high-spin ferric iron have been obtained. Quantitative analyses of the spectra have included distributions in the parameters of the spin Hamiltonian. Future goals are to understand the relation of the distributed parameters to structure, and then to understand how structure influences chemistry. Measurements at frequencies higher than X-band will provide a wealth of information, including from inter-Kramers doublet transitions. To assess the information content of high-frequency EPR spectra of iron, calculations at 9, 35,70, 95, 150 and 250 GHZ have been made for a set of parameters characteristic of the enzyme lipoxygenase. Colored, spherical dot plots have been constructed to illustrate the anisotropy of various transitions and the effects of parameter distributions on the results of these calculations.

169 MULTIFREQUENCY PULSED EPR STUDIES OF THE PRIMARY DONOR IN PHOTOSYSTEM I REVEAL A HISTIDINE LIGAND

Michelle Mac, Xiao-song Tang, Bruce A. Diner, Gerald T. Babcock and John McCracken, Department of Chemistry, Michigan State University, East Lansing, Michigan 48824 and Central Research and Development Department, Experimental Station, P.O. Box 80173, E.I. DuPont de Nemours and Company, Wilmington, DE 19880.

Photosynthesis is the process by which photochemical energy is utilized to disrupt chemical bonds in stable substrates. It requires the interplay of two pigment-protein reaction centers, Photosystems I and II (PSI and PSII). PSII is the site of water oxidation and oxygen evolution. Electron transfer between the two photosystems is mediated by a plastoquinone pool, a cytochrome bgf complex and a blue copper protein, plastocyanin. PSI, through a series of charge separations, effects the reduction of $NADP^+$. The structure of P7OO, the primary electron donor in PSI, is still controversial. Both monomers and dimers of chlorophyll a have been suggested as possible structures for Pyoo- The ligation environment of the chromophore has also been speculative. P700 the other electron transfer cofactors are located on the polypeptides encoded by the *psaA, psaB* and *psaC* genes. Three conserved histidine residues on the *psaA* and *psaB* genes are excellent candidates for binding to Pyoo- By using a histidine tolerant mutant of *Synecocystis* 6803 PCC and the pulsed EPR method of electron spin echo envelope modulation (ESEEM) we have been able to identify an axial histidine ligand to P700 d support to the dimer structural model.

170 TIME-RESOLVED ELECTRON SPIN RESONANCE STUDIES OF SPIN TRAPPING: THE REACTION OF ALKYL RADICALS WITH DMPO.

Keith P. Madden and Hitoshi Taniguchi, Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556-0579.

In situ **radiolysis time-resolved ESR studies of the reaction of 2-methyl-2-nitrosopropane (MNP) with carbon-centered radicals have shown that the trapping efficiency of this nitroso spin trap is considerably influenced by steric and electronic effects in the MNP-radical encounter complex. Rapid MNP spin trapping is observed with sterically unhindered n-alkyl radicals, while bulky branched alkyl radicals are sufficiently crowded about the radical center that second-order parent radical termination occurs in preference to radical trapping. Strongly reducing hydroxyalkyl radicals quickly react with MNP in spite of steric constraints, however, due to favorable electronic interactions between the radical and the polar N=0 moiety.**

Time-resolved experiments with the nitrone spin trap 5,5-dimethyl-l-pyrroline-N-oxide (DMPO) show that although these steric and electronic effects are still operative, their influence in DMPO spin trapping reactions is diminished relative to MNP. In the current study, the interplay of steric and inductive effects in DMPO spin trapping is examined for a series of substituted primary and secondary alkyl radicals.

171 EPR SINGLE CRYSTAL STUDY OF THE FE(m)-0-FE(ni) DIMER IN TWO SYSTEMS.

Andrzej Ozarowski and Bruce R. McGarvey, Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, N9B 3P4, Canada

EPR single crystal spectra have been obtained for the Fe(III)-0-Fe(III) dimer in $[Fe(phen)_2]_20(N0_3)_4H_20$ and $Na_4[FeEDTA]_2O3H_20$. The prominent spectrum at room temperature was found to be from the S=2 excited state. In $[Fe(phen)2]_20(N03)_4H_20$ a weaker set of lines from die S = 3 state was also characterized and in certain orientations a strong line appeared which we assumed to be from the S= 1 state. Analysis of these different spin state Hamiltonians reveals a large anisotopy in the exchange interaction between the two Fe(III) S=5/2 spins.

172 **ANGULAR AND TEMPERATURE DEPENDENCES OF SPIN-LATTICE RELAXATION IN 2D MOLECULAR COMPOSITES.** **A Niang, Guy Ablart, Jacques Pescia, Universite Paul Sabatier, 31062 Toulouse Cedex, France. Sushil K. Misra. Department of Physics, Concordia University, Montreal, Quebec H3G 1M8 Canada. R. Duplessix, N.B. Chanh, Universite de Bordeaux, 133045 Talence Cedex, France.**

We have investigated rNH3-(CH_2)4-NH_3]MX4 (or 2C4MX4) with M = Mn, Cu and X = CI, Br in monocrystalline and powdered samples over the temperature range 4.2-290 K. The relaxation time (Ti) was measured by means of the modulation method: the microwave field is amplitude modulated and an EPR signal proportional to dM_z/dt is detected in a pick-up coil coaxial with the magnetic field. So, very short *T*\ can be determined. We have measured the angular and thermal variations of Tj in the monocrystalline sample 2C4MnCl4, 2C4MnBr4 and 2C4CUCI4. The experimental data are well understood taking into account the strong exchange interaction and using the Bloembergen and Wang three-reservoir model at high temperature. *T*\ shows the same dependence for all the samples, while at low temperature its thermal variation depends on the halogen X.

173 **VARIABLE TEMPERATURE EPR STUDY OF A Ni_2CdCl6-$12H_20$ SINGLE CRYSTAL.** **Sushil K. Misra and Lucjan E. Misiak, Department of Physics, Concordia University, 1455 de Maisonneuve Blvd. W., Montreal, Quebec H3G 1M8 Canada, and Prem Chand, Department of Physics, Indian Institute of Technology, Kanpur 208016, India**

X-band (9.45 GHz) EPR spectra have been recorded on a single crystal of $Ni_2CdCl6"12H_20$ for several orientations of the external magnetic field at many temperatures in the range of 3.8-295 K. All the EPR line positions observed at any temperature were simultaneously fitted in a least-squares procedure specially developed to analyse in detail Ni^+ EPR spectra in concentrated salts, employing numerical diagonalization of the spin Hamiltonian matrix to evaluate the spin-Hamiltonian parameters gj|, gj_, and D. A detailed examination of the EPR line positions reveals that there exist two magnetically-inequivalent sites for Ni^+ in the unit cell,characterized by considerably different values of the zero-field splitting parameter (D). The intensities of the EPR lines at room temperature indicate that three Ni^+ positions in the unit cell are occupied by one set of magnetically-equivalent ions, while the other set of the inequivalent ions occupy the fourth position. The temperature dependence of D for both sets of ions is found to contain linear, quadratic, and cubic terms in temperature. The relative intensities of lines at liquid helium temperature indicate the absolute sign of the parameter D to be negative. Additional aspects of this EPR study will be presented.

174 **CONFORMATION OF DOXYL STEARIC ACID NITROXIDES IN VACUUM, WATER AND HEXANE.** **Jean M. Standard, Janeice S. Ives, and Philip D. (Reef) Morse II. Department of Chemistry, Illinois State University, Normal, IL. 61790-4160.**

Sentjurc *et al* (Arch. Bioc. Biophy. 282,207,1990) have stated that the reduction rate of doxyl stearic acid nitroxides in water depends on their conformation. They cite results which shows that 10DS is reduced more rapidly in aqueous solution than are other positional isomers (5,7,12,16). We are studying the conformation of 5,7,10, 12, and 16 DS in water, hexane, and vacuum via molecular dynamics simulation software. The Dreiding force field (Mayo, Olafson, and Goddard, J. Phys. Chem. 94,8897,1990) has been employed in adiabatic molecular dynamics calculations using the BIOGRAF program package (Molecular Simulations, Inc). Preliminary molecular dynamics simulation of 20 picoseconds for 7DS in vacuum and water indicate that the lowest energy conformation occurs when the hydrocarbon chain is folded back toward the oxazolidine with most rotations occuring between carbons 8-13. This corresponds to the decrease in order parameter observed for doxyl stearic acid nitroxides in which the oxazolidine is further along the chain (Seelig and Niederberger, Biochemistry 13,1585, 1974) and may explain the results of Sentjurc *et al*.. Molecular dynamics simulations on the remaining doxyl stearic acid nitroxides are in progress. These studies will provide information on whether the lowest energy conformations of the nitroxides differ depending on the position of the oxazolidine group on the stearic acid chain. In addition, we begin to investigate the correlation between motion, conformation, and nitroxide reduction in water by ascorbate.

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175 IMPROVED SAMPLE HANDLING FOR CELL STUDIES USING HIGH-FREQUENCY EPR.

Philip D. (Reef) Morse II* and Alex I. Smirnov, *Department of Chemistry, Illinois State University, Normal, IL.61790-4160 and Illinois EPR Research Center, College of Medicine and Dept of Chemistry, University of Illinois, Urbana, IL. 61801.

Nitroxides can be used to probe oxygen-dependent metabolic processes in cells and have been used to distinguish between normal and transformed cells. However, current methods of handling cells for EPR studies often leads to an inhomogeneous distribution of cells and local hypoxia. For example, conventional EPR techniques (X-band, 9.5 GHz) require large numbers of cells (10^7 cells in 100 ul) which may result in different zones of oxygen metabolism and misinterpretation of the correlation between oxygen concentration and nitroxide reduction. Using a W-band (94 GHz) EPR spectrometer, we have decreased sample size to 900 cells in 30 nanoliters which prevents cell crowding. Preliminary results show that 900 anoxic BHK cells reduce 100 uM perdeuterated 1% TEMPONE (2,2,6,6-tetramethylpiperidine-N-oxyl-4-one; 1.8 x 10*[2] spins in the sample) with a time constant of 511 seconds, which is slower than the time constant for the reduction of perdeuterated 1% TEMPONE observed at X-band. This suggests that cell crowding at X-band affects nitroxide metabolism. Improvements in the W-band spectrometer and handling of aqueous sample to bring the instrument close to its sensitivity for non-lossy samples (2 x 10& spins/gauss) may allow measurements of nitroxide metabolism on a single cell. **This work was supported by NIH srant R15 GM44365-01 to PDM and used the resources of the Illinois EPR Research Center (NIH Grant RR01811).**

176 CHARACTERIZATION OF MINERAL SURFACES BY EPR

Dexter D. Murphy. Martin G. Bakker, Terry Clark, Brandon Davis, Department of Chemistry, The University of Alabama, Tuscaloosa, Al 35487-0336 and, D. R. Spears, U. S. Bureau of Mines, Tuscaloosa Research Station, Tuscaloosa, Al.

Separation processes in mineral recovery based on the chemical properties of minerals, require that there exist a significant difference in the chemical properties of the minerals. Such differences could be in the types of binding sites, the energies of the binding sites and the number and distribution of such sites. Characterization of surfaces is therefore crucial in the choice of polymers, surfactants, suppressers and other reagents required to achieve a satisfactory separation. Functionalized EPR spin labels have much to offer in surface characterization. The strength and extent on adsorption of TEMPO spin probes onto the minerals chromite and forsterite is dependent upon the functional group (NH2, OH, COOH) attached to the TEMPO. Adsorption from cyclo-hexane, followed by evaporation, showed significant probe aggregation on the surface. Subsequent studies of frozen cyclohexane slurries indicate that the aggregation observed results from precipitation of the spin probe. Interaction of the mineral surfaces with the spin probes is apparent in the different coupling constants and different rotation mobilities observed. The correlation between the slurry work, and the adsorption isotherms and the implication for binding of surfactants and polymers to surfaces will be discussed.

477 CHARACTERIZATION OF CALCIUM BINDING SITES IN THE KIDNEY STONE INHIBITOR GLYCOPROTEIN (NEPHROCALCIN) WITH VANADYL ION BY EPR AND ENDOR SPECTROSCOPY. **Devkumar Mustafi and Yasushi Nakagawa, Dept. of Biochemistry and Molecular Biology, The University of Chicago, 920 East 58th Street, Chicago, IL 60637.**

Nephrocalcin (NC), a calcium oxalate monohydrate crystal growth inhibitor (kidney stone inhibitor) glycoprotein of 14000 molecular weight, is a Ca^{2+} binding protein. NC was isolated from bovine kidney tissues and purified by using DEAE-cellulose chromatography into four fractions A, B, C, and D. They differ according to the extent of phosphorylation of serine side chains and the *y*-carboxyglutamic acid content. Fractions A and B exhibit strong calcium oxalate monohydrate crystal growth inhibition whereas fractions C and D inhibit crystal growth weakly. Fraction A with the highest Ca^{2+} binding affinity was characterized with respect to metal binding sites using the vanadyl ion ($V0^{2+}$) as a paramagnetic probe in EPR and ENDOR spectroscopic studies. At pH 6.0, unbound $V0^{2+}$ is EPR silent, and the EPR signal intensity is proportional to the amount of complexed $V0^{2+}$. Fraction A of nephrocalcin bound $V0^{2+}$ with a stoichiometry of 4 g-ions of $V0^{2+}$ per mole of protein that was competitive with Ca^{2+}. No solvent molecules could be detected in the inner coordination sphere of $V0^{2+}$ and only protein residues could be detected by ENDOR as ligands to the metal ion. This type of binding environment differs significantly from the binding sites in other types of calcium binding proteins by the complete exclusion of water molecules in the inner coordination sphere. (Supported by GM 21900).

178 AN EVALUATION OF NEW CARBONACEOUS OXYGEN-SENSITIVE EPR PROBES. **Shong-Wan Norbv*. Anthony A. Lizzio, Robert B. Clarkson\ 'Department of Veterinary Clinical Medicine, Illinois EPR Research Center, University of Illinois, 506 S. Mathews, Illinois State Geological Survey, 615 E.Peabody Dr., Urbana, IL 61801.**

The application of carbonaceous materials, natural or synthetic, as oxygen sensitive probes for EPR oximetry has been well documented. For specific biological studies, there is a need for probes of much greater sensitivity and shorter response times. Hence, we have evaluated a variety of carbonaceous materials in order to develop a suitable probe for these studies. The properties of the samples tested include surface area, oxidation, activation, ash quantity, heat treatment, hydrophobicity and polarity. Initially, each sample was exposed to nitrogen and subsequently to air; samples showing a significant change in EPR linewidth under the two experimental conditions were tested next for sensitivity to oxygen in an aqueous environment. Our data indicate that for many carbohydrates and coal based materials, maximum heat-treatment temperatures in the region of 600°C produced the most oxygen-sensitive chars. A KOH treated sample exhibited a single- line EPR spectrum with broad and narrow components. Oxidation eliminated the broad component. Carbosieve®, a commercial sample, seemed to be the most oxygen sensitive probe among all samples tested. However, this sensitivity was greatly reduced in an aqueous environment. Partial support from NTH (GM 42208 and RR01811).

179 EPR INVESTIGATION ON PHOTO-IRRADIATION AND ANISOTROPIC HYPERFINE INTERACTION OF VANADIUM BRONZES, **Keiichi Ohno, Yasuyuki Morita, and Yoshikazu Kaneko , Department of Information Engineering, The Polytechnic University, Sagamihara, Kanagawa 229, Japan, *Institute of Inorg. Synthesis., Faculty University of Engineering, Yamanashi University**

Nonstoichiometric compounds formulated chemically as MXV2O5 (M= an alkali metal, copper, or silver) are called vanadium bronzes. General feature of these oxygen-vanadium bronze compound is that the outer shell electrons of the M atom transfer into the unfilled d-shell of the vanadium ions. The metal M ions themselves in the oxygen tunnels of lattice, releasing inside a chain of similar polyhedra p, electrons which occupy equivalent orbitals, predominantly d, and move between them by a hopping mechnism. EPR measurement were performed for P-LixMyV205(M=CaJ3a,Sr) from room temperature down to about 5K to investigate the roles of electron and ions for electric conductivity and photochromism. Almost spectra contain only slightly asymmetric broad singlet lines (AHpp«20mT) which are nearly independent of temperature except for p-Bao.nV205. The linewidth of the latter compound decreases with decreasing temperature. The anisotropics of g-factor were examined for P-Lio i8Sro 09V2O5 compounds because they formed small but useful single crystals for the measurement.

1g0 **EPR AND EPR IMAGING OF PHTHALOCYANINE-LI SINGLE CRYSTAL USING A MICROCOIL,** **Keiichi Ohno, Yasuyuki Morita, Masaaki Aoyama and Masao Kohno , Department of Information Engineering, The Polytechnic University, Sagamihara, Kanagawa 229, Japan, *Yamagata Technopolis, Yamagata, Japan, ESR Group Appl. Lab. Analyt. Instrum., JEOL, LTD, Tokyo, Japan**

EPR spectra of Pc-Li have extraordinarily narrow Lorentzian line shapes (g=2.0020, AHpp=2.5p.T for a single crystal and g=2.00168, AHpp=T0uT for a polycrystalline sample) at room temperature under vacuum. The resonant lines change to ones with g=2.00188, AHpp=77pT with the introduction of air, the property of which is made use of to attempt the development of oximeters. A microcoii was attached at the top of a capillary for chromatography (i.d.,250um, o.d.,360u,m), which was passed through a central tube used as a center conductor of a semi-rigid cable. The capillary gets out of the tube at a micro strip line which was interposed in the middle of the semi-rigid cable. An optical fiber (o.d.,250 pm), was inserted in the capillary as a plunger to keep liquid sample or draw in a solid sample. To introduce oxygen gas into the microcoii and prevent it from any liquid, air-transparent film adhered on the surface of a polymer tube which two windows were cut. The typical dimension and weight of a Pc-Li single crystal used here were 0.03x0.03x1 iW and about 1 pg. Oxygen gas pressure was controlled from 0 to 30 mmHg and at atmosphere. ESR spectra were measured, which converted from an absorption line shape to emission one after the introduction of air. The detector was applied to biological samples.

181 **NITROXIDE SPIN PROBE/LABEL STUDY OF HYDROGEN BONDING AND PROBE SIZE EFFECTS IN A LINEAR POLYMER** **M. D. Pace and A. W. Snow, Code 6120, Naval Research Laboratory, 4555 Overlook Ave, S. W., Washington, D. C. 20375-5342**

An electron paramagnetic resonance (EPR) nitroxide spin-probe/spin-label study was performed on a linear polymer of diglycidyl ether bisphenol A (DGEBA) over the temperature range from 30°C to 200°C. The spin probes used in this study include four monomer nitroxides: TAMINE, BZONO, TEMPOL, and TEMPO (respectively, 4-amino-, 4-benzoyloxy-, 4-hydroxy- and unsubstituted 2,2,6,6-tetramethyl-piperidine-l-oxyl), two model compounds having structures similar to the repeat unit of the polymer (denoted PGETA and CPGETA), and the nitroxide spin labeled DGEBA/CHA copolymer. From the EPR spectra, the temperatures at which the motionally averaged ^{M}N-hyperfine coupling is *ca.* 2.5 mT (defined as T_{50}) was determined for each of the spin labeled samples. TAMINE, TEMPOL, and TEMPO probes show a T_{50} temperature dependence which is attributed to hydrogen bonding.

182 **PROGRAMMABLE TIMING UNIT,** **Richard W. Ouine. Department of Engineering, University of Denver.**

A Programmable Timing Unit (PTU) has been developed primarily to control system timing in EPR ESE experiments, but could find broader use in general purpose timing applications. The PTU has a variety of operating modes and is programmed from a PC using software developed in Visual BASIC. The PTU has 1 ns resolution and is capable of generating multiple outputs, including controls for microwave switches, phase shifters, boxcar averagers, and scope triggers. Unique features of this unit are extraordinary flexibility realized through a programmable matrix design and 1 ns resolution realized through a special calibration technique that compensates for errors in individual digital delay generator circuits.

183 MULTIPLE FREQUENCY EPR STUDIES OF NOVEL COMPOUNDS WITH TWO WEAKLY COUPLED SPIN = 1/2 METAL CENTERS. Arnold M. Raitsimring, Partha Basu and John H. Enemark. Department of Chemistry. University of Arizona, Tucson, Arizona 85721.

The modified tetraaryl porphyrins (3,4-OH-TTP) and (2,3-OH-TTP) possess a single pendant catechol group that can coordinate to the $LMo^{V}O^{2+}$ unit (L = hydrotris(3,5-dimethyl-l-pyrazolyl)borate). A variety of spin 1/2 metal centers can then be inserted into the porphyrin center to produce compounds of the type M(3.4-Mo-TPP) and M(2,3-Mo-TPP) that contain two spin = 1/2 metal centers separated by about 9.4 and 7.9 **A,** respectively. For M = Cu" and low spin Fe , the weak Mo-M coupling has been measured at Q,X,S, and L band EPR frequencies at 16,77 and 120 K. Of particular interest is the weak anisotropic dipolar coupling in $Fe(/v\text{-}Melm)_2$(3,4-Mo-TPP)CI, a model for the inter-prosthetic group interaction in the enzyme sulfite oxidase. The comparison of experimental and simulated spectra of M(3,4-Mo-TPP) compounds has allowed the relative orientations of the two spin centers to be obtained. For M(2,3-Mo-TPP) compounds the values of exchange interactions have been evaluated.

Q,S,L-band measurements were done at the National Biomedical ESR Center (supported through NIH RR01008) with the kind permission of Professor SJ.Hyde. We thank Dr. C. Felix for assistance with the multiple frequency measurements and NIH (GM-37773 to JHE) and NSF (DIR-9016385) for financial support.

184 **PRELIMINARY RESULTS OF THE STUDY OF Tb^{3+} PHASE RELAXATION IN THE SILICATE GLASS.** **Igor A.Gromov, Sergei B.Orlinskii Raf a. 11 H. Rakhrnatu 11 in , Urii K. Rosen t.avaig, MRS Laboratory, Kazan State University, 420008, Kazan, Tatarstan, Russia**

Temperature and concentration dependences of the phase relaxation rate of T_m of Tb ions have been investigated in the silicate glass. In the temperature dependences of T_m the temperature independent regions and linear temperature dependences have been observed. The first can be explained by dipole-dipole interactions. The second has been observed earlier and probably are typical for glasses, but it has not been explained so far. The interpretation of concentration dependences of T_m are most difficult due to many types of sites in the glass. Contributions of different types of Tb centers in EPR change with temperature. The phase relaxation study in addition to the information on the spin dynamic can help separate different types of Tb^{+} sites in the glasses.

185 **ELECTRON SPIN ECHO DECAY: A PROBE OF ELECTRON-ELECTRON SPIN-SPIN INTERACTION IN SPIN-LABELED IRON PORPHYRINS.** **Margaret H. Rakowskv. Gareth R. Eaton, and Sandra S. Eaton, Department of Chemistry, University of Denver, Denver, CO 80208.**

Nitroxyl free radical electron spin relaxation times were examined between 5 and 70 K by two-pulse spin echo spectroscopy for four spin-labeled complexes of low-spin iron(ffl) porphyrins. At low temperature the iron electron spin lattice relaxation rate (LTi) is slow compared with the electron-electron spin-spin sphtting. However as temperature is increased, *fy* becomes comparable to the spin-spin splitting, which causes a collapse of the splitting in the continuous wave EPR spectra and an increase in the nitroxyl spin echo decay rate. The temperature dependent changes in the spin echo decays were analyzed to determine the interspin distance, r, the exchange coupling constant, J, and Tj for the low-spin iron. Values of were in good agreement with those obtained directly by saturation recovery. The analysis of the nitroxyl spin echo data also provided values of the iron Ti at temperatures where the electron spin-lattice relaxation rate was too fast to measure directly by saturation recovery. These data demonstrate the utility of spin echo measurements as a probe of electron-electron spin-spin interaction with a relatively rapidly relaxing metal ion such as low-spin Fe(III).

186 **ESE-ENDOR OF ORIENTATIONALLY DISORDERED MANGANESE COMPLEXES.**

David W. Randall. Bradley E. Sturgeon, James A. Ball, R. David Britt,* Department of Chemistry, University of California, Davis, Davis, CA 95616. (916) 752-6377

Proteins containing multinuclear manganese clusters are of biological importance. Among those proteins utilizing this motif are the oxygen evolving complex (OEC) of photosystem JJ which photosynthetically produces molecular oxygen and the manganese catalase enzyme which catalyzes disproportionation of hydrogen peroxide. Understanding the electronic structure of a redox active manganese cluster may provide insight into enzymatic mechanisms used in these systems. Such insight can be provided by obtaining hyperfine and nuclear electric quadrupole coupling constants using the pulsed ENDOR technique. We have explored ^{55}Mn ENDOR by studying orientationally disordered Mn^{2+} systems possessing varying amounts of zero field splitting. The large hyperfine interaction of Mn allows resolution of EPR transitions originating from each of the six mj levels of the ^{55}Mn nucleus. With such a hyperfine resolved EPR spectrum, ENDOR spectra can then be collected in which a subset of ENDOR transitions are induced. This m/ EPR selection observed in the ENDOR of mononuclear systems is also observed in ENDOR data from multinuclear metal clusters of biological interest. One class of spectral models is based on an antiferromagnetically exchange-coupled dimer containing a di-^f-oxo bridged manganese (HI, IV) unit. The EPR spectra of these models are similar to those of the biological samples mentioned above. Pulsed ^{55}Mn ENDOR obtained while selecting mj states of this model compound has aided in the interpretation of the data. Spectral simulations allow us to assign the hyperfine and quadrupolar interactions of both manganese nuclei. Additionally, ^{55}Mn ENDOR results from both manganese catalase and OEC will be presented.

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A SYSTEMATIC APPROACH FOR STUDYING CU IMIDAZOLE INTERACTIONS USING MULTI-FREQUENCY ESEEM; APPLICATIONS TO CU-BLEOMYCIN.

Pieter J. van Dam, Eduard J. Reijerse, and Engbert de Boer, Department of Molecular spectroscopy, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Many Copper containing proteins exhibit wel denned ESEEM signals detected at X-band and C-band. In these systems the Cu(II) ion is coordinated with one or several histidine residues. The main sharp features measured in the ESEEM spectra originate from the interaction with the remote nitrogen of the imidazole ring. These so-called 'NQI' features provide information about the magnitude and orientation of the Nuclear Quadrupole interaction (NQI).

We present a systematic approach to determine the constraints of the euler angles a, /?, 7 of the NQI tensor in the g-tensor principle axis system. The first step is to analyze the intensity ratios of the quadrupole peaks and the lineshape of the double quantum feature measured on a canonical position in the EPR spectrum. This will lead to a constraint in the angles (/?, 7) as well as the effective hyperfine interaction. This information is further refined using spectra on other orientation selective positions. We have applied this method to Cu-Bleomycin and a modelcompound Cu-A'-(2-(4-imidazolyl)ethyl)pyridine-2-carboxamide (Cu-pypep) and determined principle quadrupole values and the orientation of the quadrupole tensor with respect to the g-tensor axis system. The measured NQI parameters (Cu-Bleo K=1.38 MHz, ?7=0.90; Cu-pypep K=1.43 MHz, *T)=0.89)* are almost identical. De angle *j3* was determined for both Cu-Bleo (ȷ3 = 36°) and Cu-Pypep (0 = 29°) and compared to the value derived from the crystal structure of Cu-Pypep (/? = 25°). The constrains between *a* and 7 will also be presented.

188 NEW INSIGHT INTO THE STRUCTURE OF NITROSYL HEMOGLOBIN AND ITS MODEL COMPOUNDS AS STUDIED BY ESEEM.

Sergei A. Dikanov[1], Alexei M. Tyryshkin[1], Edward J. Reijerse[2], Christian Burgard[3], and Jurgen Huttermann[3]. (1) Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia. (2) Department of Molecular spectroscopy, University of Nijmegen, Netherlands (3) Fachrichtung Biophysik, Universitat des Saarlandes, Homburg/Saar, Germany.

Nitrosyl (NO) ligated hemoglobin (HbNO) is considered as a useful model to provide insight into the biochemistry of oxyhemoglobin. Many details of the electronic structure of the NO-bound heme species remain, however, unclear. We present new data on the structure of NO-hemoglobin as obtained by orientaton selective Electron Spin Echo Envelope Modulation Spectroscopy (ESEEM). This techniques turns out to be very sensitive to the electron-nuclear interaction parameters for the equatorial nitrogens of the pyrrole ligands which are too weak to be observed using CW-EPR. Several biological heme species were investigated: a) The isolated *a* and *(3* chains of NO-hemoglobin, b) the two hybrids of hemoglobin with asymmetrically ligated chains: (a-NO, /3-CO) and vice versa, c) NO ligated hemoglobin in two quaternary (R/T)-states, and d) NO-ligated myoglobin. These species exhibit ESEEM spectra which can be interpreted using an identical NQI-tensor for all compounds (K=0.43 MHz, n=0.39). These values differ slightly from those obtained for a series of NO-Fe(TPP)-Imidazole model complexes (K=0.47, TJ=0.45). Apart from the pyrole nitrogen signals, also additional ESEEM features were observed. These are still unidentified but may be connected with the axial coordination of Histidine F8. It turns out that the ESEEM spectra of all biological compounds can be composed as linear combinations of the ESEEM spectra of the isolated hemoglobin chains! These findings strongly support the "two conformation model" of NO-heme proteins proposed by Morse and Chan [1]. Also, new conclusions can be drawn about the cooperative effect of NO/02 binding.

[1] R.H. Morse and S.I. Chan. J. Biol. Chem., 255:7876, 1980.

189 L-BAND LOOP GAP RESONATOR DESIGN FOR LOW-TEMPERATURE EXPERIMENTS,

George A. Rinafd. Barnard Ghirn, Gareth R. Eaton, Departments of Engineering and Chemistry, University of Denver, Denver, CO 80208.

An L-band (1-2 GHz) loop gap resonator designed for ease of sample change and tuning at low temperature has been constructed of copper. The LGR and tuning assembly is designed to fit in an Oxford 935 liquid helium cryostat. An LGR with a resonant frequency of about 1 GHz had a room temperature loaded Q of 350. Tuning is accomplished with a variable capacitor, which can be adjusted remotely while at low temperature. The tuning range is sufficient to critically couple the LGR for CW and saturation recovery operation and to strongly overcouple the LGR for spin echo operation.

190 MAGNETIC PROPERTIES OF TRIPLET COPPER(II) AND OXOVANADIUM(IV) PORPHYRIN CATION RADICAL COMPLEXES

Minoru Satoh, Keiko Ise, Fujio Ebina, Yasunori 0hba\ Seigo Yamauchi*, Mikio Hoshino'*, and Masamoto IwaizumiMbaraki College of Technology, 866 Nakane, Katuta, Ibaraki, 312 Japan; *:Institute for Chemical Reaction Science Tohoku University, * *:The Institute of Physical and Chemical Reaearch.

The copper(II) and oxovanadium(IV) porphyrin cation radical complexes were examined by EPR spectroscopy. The cation radical complexes having bulky peripheral substituents are present as a monomer in fluid solution and show EPR spectra due to the intramolecular triplet state, but the cation radical complexes having no such substituents form a dimer in solution. On the other hand, when they are oxidized in frozen solution by y-ray irradiation, the cation radical complexes are always formed as a monomer. The copper(II) porphyrin cation radical complexes are clasified into two groups by the | D | and 2J values, one has small I D | and small negative 2J values, while the other group has large | D | and large negative 2J values. These I D | and 2J values seem to show good correlation with the electronic configuration of the porphyrin radical complexes. They are well explained by assigning the A2u type electronic configuration to the former type complexes and the Alu type to the latter type complexes. On the other hand, oxovanadium(IV) porphyrin cation radical complexes are also clasified into two types, according to magnetic properties, which may be related to the electronic configurations, Alu and A2u. The A2u radical complexes are more antiferromagnetic than A2u type radical complexes, though the two types of radical complexes have nealy equal | D | values.

191 **THE THREE-TERM MODEL FOR FERRIC IRON AND G-STRAIN EPR SIMULATIONS: DISTRIBUTIONS OF CRYSTAL FIELD PARAMETERS.** **Charles E. Schulz. Department of Physics, Knox College, Galesburg IL, 61401 and Peter G. Debrunner, Department of Physics, University of Illinois at Urbana-Champaign, Urbana IL, 61801.**

The ferric ion in metalloproteins exists in a variety of spin states: S=5/2, 3/2, and 1/2 (or quantum mixtures of these states.) Crystal field models have been developed to describe each of these states in isolation, but a more general Three-Term Model (TTM) as described by Harris *(J.Chem.Phys.* 48, 2191 (1968)) and Ristau *(PeriodBiol.* £1, 39 (1981)) describes all possible admixtures of these states with a small number of physically meaningful parameters. The "g-strain" broadening of ferric EPR spectra can be attributed to a distribution of micro-conformations of the iron site which is in turn describable by a distribution of crystal field parameters. We have developed an algorithm for calculating g-strain EPR spectra using the TTM, and have applied it to simulation of various low-spin, mixed-spin, and high-spin ferric systems. This g-strain model 1) predicts a linewidth variation with angle which is not describable by a linewidth tensor, 2) explains in a natural way observed linewidth differences among the g-tensor principal axes, and 3) results in a realistic interpretation of g-values for systems which, like low-spin P450, require an orbital reduction factor k>l.0 in the standard one-term model.

192 **THE COORDINATION OF COPPER IONS TO HYDROXAMATE BINDERS.**
V. Kofman, J.J. Shane, S.A. Dikanov, A. Haran, J. Libman, A. Shanzer and D. Goldfarb. Chemical Physics and Organic Chemistry Departments, Weizmann Institute of Science, Rehovot, Israel and the Institute of Chemical Combustion and Kinetics, Novosibirsk, Russian Federation.

Dipodal chiral dihydroxamate ion binders create a cavity with four oxygens available for binding a cation. The ligands contain two nitrogens in the second coordination shell of the cation. We have used orientation selective ESEEM and HYSCORE spectroscopy as tools to study the binding geometry of copper ions to these ligands. The ESEEM experiments, carried out at 8.4 and 9.2 GHz show that the isotropic hyperfine coupling is in the range of exact cancellation leading to narrow lines in the Fourier Transform (FT) ESEEM spectrum, from which we estimate $|A_{iso}|$=1.3MHz, $|e^2qQ/h)$=3.9MHz, r|=0.83. Several combination peaks arising from the presence of two nitrogen nuclei were also observed. Surprisingly, we found not only combination lines from peaks assigned to the same manifold but also a peak interpreted as a combination line from different manifolds. The HYSCORE spectrum should show only cross-peaks between frequencies from different manifolds, but we also found peaks apparently arising from correlations within one manifold. We have constructed several models to explain the observed cross-peaks and combination peaks and we have carried out spectral simulations to account for the orientation dependent FT-ESEEM spectra and test the various models. These will be presented and discussed.

193 DESIGN OF A VERSATILE PULSED ENDOR SPECTROMETER. J.J. Shane. D. Goldfarb and S. Vega. Chemical Physics Dept. Weizmann Institute of Science, Rehovot 76100, Israel.

The design of a new pulsed ENDOR spectrometer currently under construction in our laboratory will be reported on. The design features a new pulse generation system based on an Interface Technology RS690 word generator combined with Stanford DG535 digital delay generators, giving the high time resolution needed for the microwave pulses (<1ns). The microwave pulse bridge combines two microwave sources operating at 8.5-9.6 and 8-12 GHz. A two-channel pulse former unit with 4-step phase switching on each channel and a low-power pulse arm bypassing the TWTA, allows for a range of pulsed EPR experiments. The RF-part of the spectrometer incorporates two independent channels with output frequencies between 0 and 200 MHz. High-speed phase and amplitude switching of the RF signals is achieved through a new design incorporating two RF synthesizers for each channel. The output of a PTS X10 synthesizer, operating at 70-80 MHz and capable of 1 microsecond phase switching, is connected to a high-speed constant-phase digital attenuator. The resulting signal is mixed with the output of a PTS 160 synthesizer, extending the frequency range to 0-200MHz. Unwanted leakage signals and the second mixer output frequency are removed by several output filters. The combined output signal of the two RF units is amplified to KW levels. A passive feedback circuit is used to level the output pulse-power. A very interesting but as yet unexplored application is the study of radicals in solution by combining pulsed ENDOR and Fourier Transform EPR.

194 **THERMAL PHASE TRANSITIONS IN DPPC LIPOSOMES AS STUDIED BY HIGH-FREQUENCY EPR.** **Alex I. Smirnov, Tatyana I. Smirnova, and Philip D. (Reef) Morse II*. Illinois EPR Research Center, College of Medicine and Dept of Chemistry, University of Illinois, Urbana, IL. 61801 and *Department of Chemistry, Illinois State University, Normal, IL. 61790-4160.**

EPR spin-probe studies of thermal phase transitions in liposomes are usually carried out at X-band (9.5 GHz). X-band studies suffer from low spectral resolution; for non-deuterated nitroxides, only the high-field component is split. Better resolution, as well as measurement of rotational correlation times, can be obtained only with specially designed nitroxides. In the present work, we demonstrate and discuss the prospects of high-frequency (95 GHz) EPR for obtaining rotational and partitioning information about spin probes in lipid systems. We monitored the thermal phase transition for aqueous dispersions of the phospholipid DPPC (1,2-dipalmitoyl-OT-glycero-3-phosphatidylcholine). At all studied temperatures, the nitroxide spin probe TEMPO (2,2,6,6-tetramethylpiperdine-l-oxyl) partitioned between both membrane (hydrocarbon) and aqueous phases. W-band completely resolves the entire TEMPO EPR spectrum in both aqueous and hydrocarbon environments. Therefore the TEMPO partition coefficients can be determined with better accuracy at W-band. The more informative high frequency EPR data were analyzed using a fast rotational model to derive the rotational correlation times during the thermal phase changes in the DPPC membrane. **This work was supported by NIH grant R15 GM44365-01 to PDM and used the resources of the Illinois EPR Research Center (NIH Grant RR01811).**

1g5 **RAPID QUANTITATION OF INHOMOGENEOUSLY BROADENED EPR SPECTRA BY A FAST CONVOLUTION ALGORITHM.** Alex I. Smirnov[1] and R. Linn Belford[1-2], Illinois EPR Research Center, [1]College of Medicine and [2]department of Chemistry, University of Illinois, 506 S. Mathews, Urbana, IL 61801.

Spectral simulation and optimization of simulated parameters to fit experimental data are very powerful tools for data analysis in EPR spectroscopy. Recently, Halpern and coworkers developed a fast algorithm for quantitation of inhomogeneously broadened EPR spectra *(Volgt* lineshape). They approximated the Voigt profde by a sum of Lorentzian and Gaussian functions and used the Levenberg-Marquardt algorithm for multidimensional optimization. We describe an even more accurate and flexible approach to linewidth simulation based on a fast convolution algorithm (FCA). FCA was also applied for calculating the partial derivative matrix required for Levenberg-Marquardt optimization. All fitting parameters, including dispersion contribution, and Lorentzian and Gaussian linewidths are extracted directly. A fixed hyperfine and/or superhyperfine pattern may be included in the fitting procedure without significantly increasing computational time. We show application of this technique to extract Lorentzian broadening of a CTPO EPR spectrum at various oxygen concentrations and to study the penetration of a 1.13 GHz microwave field into a lossy dielectric sample. The work used the resources of the Illinois EPR Research Center (NTH Grant RR01811). Some elements of software package used in this work were provided by Scientific Software Services (Bloomington, IL).

196 **EPR IMAGING OF NATURAL FREE RADICALS IN ROASTED COFFEE BEANS.** Alex I. Smirnov[1]. and Philip D. (Reef) Morse[2], II, Illinois EPR Research Center, [1]College of Medicine, University of Illinois, 506 S. Mathews, Urbana, IL 61801, and [2]department of Chemistry, Illinois State University, Normal, IL, 61790-4160.

Usually, the concentration of free radicals naturally occurring in food products is low and is undetectable by EPR. However, higher concentrations of free radicals in food can be generated during processing - for example, during y-sterilization and/or roasting. While conventional EPR is useful in characterization and quantitation of paramagnetic centers in the food, EPR Imaging can provide information on the distribution of these paramagnetic centers. As an example, we have measured the distribution of spins in roasted coffee beans obtained from a local supermarket. The experiments were carried at X-band (9.5 GHz) with the aid of a commercial EPR Imaging software package (ImageWare, Scientific Software Services, Bloomington, IL). The beans exhibit a strong single-line EPR spectrum of 6 G linewidth. Maximum entropy deconvolution was used to improve the spatial resolution of the image. The reconstructed 2-dimensional images correspond to the geometrical shape of the beans. Thus, the EPR Imaging method can be useful in monitoring the spatial distribution of radicals formed during food processing. This work used the resources of the Illinois EPR Research Center (NTH Grant RR01811).

197 **W-BAND (95-GHZ) EPR OF NITROXIDES WITH COMPLEX SUPERHYPERFINE STRUCTURE: FAST MOTION.** Tatvana I. Smirnova. Alex I. Smirnov, and R. Linn Belford. Illinois EPR Research Center, University of Illinois, 506 S. Mathews, Urbana, IL 61801.

The utility of multifrequency and very high frequency EPR for full determination of the rotational diffusion tensor was recently demonstrated by Freed and coworkers for selected nitroxides in toluene -d_g solvent. In this work we extend this approach to the nitroxides with a complex superhyperfine structure such as 3-doxyl-17P-hydroxy-5a-androstane (probe 1) and 3-maleimido-PROXYL (probe 2). o-xylene was used as a solvent. Even at a relatively long rotational correlation time, T = 10*[9] sec, the X-band EPR spectra do not reveal any motion effects because of a complex superhyperfine (shf) pattern. At 95 GHz (W-band), the range of rotational correlation times measured by EPR is extended by a factor of 10 towards short times compared with 9.5 GHz., producing a more pronounced motional effect on the linewidth at the same correlation times. The shf is purely resolved at W-band, but it contributes significantly to the inhomogeneous linewidth and makes direct estimation of T inaccurate. We use shf information from the X-band spectra in order to improve the accuracy of T determination. The linewidth parameters are extracted from W-band spectra via Levenberg-Marquardt optimization under the assumption of a fixed shf pattern. Microwave phase effects are directly included in the fitting algorithm. Results are analyzed in terms of anisotropic Brownian diffusion theory. This work was partly supported by NTH Grant GM-42208 and used the resources of the Illinois EPR Research Center (NTH P41-RR01811).

198 EPR OF SOME VEDRAZYL FREE RADICALS: LOW DIMENSIONAL BEHAVIOR. **Alan Katritzky[1], Tatvana I. Smirnova[2], Sergei Belyakov[1], R. Linn Belford[2], and Naresh Dalai[3], [1]Department of Chemistry, University of Florida, Gainesville, FL 32611, Illinois EPR Research Center and Department of Chemistry, University of Illinois, Urbana, IL 61801, department of Chemistry, West Virginia University, Morgantown, WV 26506-6045.**

Vedrazyl free radicals are a family of compounds with attractive organic/molecular ferromagnet properties. Previous studies have shown that the linewidth of a single- line EPR spectrum from polycrystalline vedrazyl samples varies with the molecular structure. EPR linewidth data at various temperatures correlate with magnetic susceptibility revealing a ferromagnetic phase transition at low temperatures. In the present work we examine angular variation of EPR linewidth of some novel types of vedrazyl radicals available in a crystal form. Observed linewidths have a "W-shape" angular dependence that is characteristic for low-dimensional (1- or 2-D) spin systems. Linewidth angular dependence was used to separate secular and nonsecular contributions to the EPR lineshape. EPR can reveal the low-dimensionality of the spin system even at room temperature, while magnetic susceptibility data in a wide temperature range are required to provide a basis for assigning a certain model for the spin-spin interactions in the system. **A. K. and S. B. thank the US Army Research Office (Contract DAAL03-92-G-0195) for support. This work used the resources of the Illinois EPR Research Center (NTH P41-RR01811).**

199 HALF-FIELD EPR TRANSITIONS IN SYNTHETIC CARBOHYDRATE CHARS. **Tatvana I. Smirnova. Alex I. Smirnov, R. B. Clarkson, and R. Linn Belford. Illinois EPR Research Center, University of Illinois, 505 S. Mathews, Urbana, rL, 61801.**

Half-field EPR transitions (g=4.00) are observed in some synthetic carbohydrate chars prepared by heat-treatment at temperatures less than 620 C. The half-field line has a lineshape similar to that of the main resonance and about the same intensity at transverse and longitudinal microwave excitation. Its relative intensity decreases with increasing char heat-treatment temperature. In contrast, no g=4 transitions were detected for chars synthesized at temperatures greater than 620 C. The ratio of intensity of the half-field transition to that of the main resonance is about 10^{-6} and does not change from 4.5 to 55 K. At 4.5 K, the g=4 line has about half of the linewidth of the main resonance. Relative intensity of the half-field signal decreases with increasing heat-treatment temperature while spin density increases. The observed half-field resonance can be explained by existence of isolated aromatic radical clusters or by a low-dimensional spin-exchange network within the solid. **This work was supported by NIH (GM 42208). Research resources were provided by NIH (P41-RR01811).**

200 NEAR OPTIMAL PROJECTION ANGLE SELECTION BY MINIMUM ENTROPY CRITERION IN EPR IMAGE RECONSTRUCTION. **G.Placidi, M.Alecci, A.Sotgiu. Dip. Scienze e Tecnologie Biomediche - Universita' dell'Aquila, Via Vetoio, 67100-L'Aquila, ITALY.**

Image reconstruction from projections is based upon calculations on a set of spectra collected at different orientations of the field gradients. It has been shown (I.J.Kazantsev, Inverse Problems, 7,1991) that the reconstruction algorithms give different results when used on different sets of projections of the same sample. This is because distinct projections have different information content. In the absence of any *a-priori* knowledge of the sample shape and symmetry, a regular set of orientations is necessary. We have studied an objective acquisition method based on an information function related to the entropy of the projections. In this way, the information content of the different projections can be determined and more infonnative set of projections selected. The information function is evaluated during the acquisition and, on the basis of a first group of measured projections, subsequent acquisition angles can be selected. The acquisition of new projections between two adjacent directions ends when the difference in the information function is smaller than a given value. Simulated and experimental data show that, for an equal number of projections, the results obtained using this information function are consistently better than those obtained using a regular set of projections.

201 REGIONAL NITROXIDE FREE RADICAL IMAGING BY LOW FREQUENCY (280 MHZ) EPR SPECTROSCOPY IN WHOLE RAT. **Antonello Sotgiu, Marcello Alecci, Marco Ferrari, Valentina Quaresima, and Cinzia L. Ursini Dip. Scienze e Tecnologie Biomediche, Universita' dell"Aquila, Via Vetoio, Coppito, 67100-L'Aquila, Italy**

An electron paramagnetic resonance (EPR) spectroscopy and imaging apparatus at radio frequency (280 MHz) has been used to localize a pyrrolidine nitroxide free radical simultaneously in selected regions of whole rat (lower abdomen, liver and thorax). The nitroxide 2,2,5,5,-tetramethylpyrrolidine-l-oxyl-3-carboxylic acid (PC A) had a whole body monoexponential decay with half life of 23 ±12 (n=6) min for 3 mmol/kg PCA. One dimensional (1-D) longitudinal projections were collected on rats in the presence of 8-15 mT/m field gradient. With an injection dose of 3 mmol/kg, PCA half lives were similar in the lower abdomen and in the liver (19 ± 1 and 17 ± 2 min), but significantly longer (22 ± 2 min) in the thorax. Sequential two-dimensional (2-D) images of PCA distribution in a plane longitudinal to the rat body were obtained in the presence of a gradient of 12 mT/m (acquisition time 5 min; resolution 8 mm). Few min after injection the nitroxide was detectable in the left side of the thorax area, but it was mostly localized in the liver. PCA was more uniformly distributed in the image collected after 17 min. Time resolution (25 s) limits the applicability of our EPRI technique. The ongoing development of RF pulsed at low frequency should reduce the acquisition time to the ms range allowing three dimensional images of nitroxide in whole rat.

202 TIME-RESOLVED EPR STUDY OF THE PHOTOEXCITED TRIPLET STATE OF C_{60} ADSORBED ON SILICA GEL. Carlos A. Steren, Hans van Willlgen and Marco Fanciulli, Dept. gf Chemistry, University of Massachusetts at Boston, Boston, MA 02125; Institute of Physics and Astronomy, Aarhus Univ., Dk-8000 Aarhus C, Denmark.

The photoexcited triplet state of C_{60} (*C60^ absorbed on silica gel has been studied with FTEPR and cw-EPR techniques. The transient EPR spectrum of *CgQ was measured as function of time after the laser pulse. The analysis of the data gives information on the dynamics of the C^q molecule on the silica surface. The effects of C,„ concentration and of the presence of solvent in the silica gel pores were analyzed. THe results will be related to those given in the literature for in liquid and frozen solutions.

203 DISTORTION OF EPR SPECTRA DUE TO MATERIALS WITH HIGH DIELECTRIC LOSS, **Minoru Sueki. George A. Rinard, Gareth R. Eaton, and Sandra S. Eaton, Department of Chemistry, University of Denver, Denver, CO 80208.**

CW and spin echo EPR signals were recorded for DPPH and irradiated fused quartz samples at the center of a sphere of solvent in an X-band TEJO2 rectangular cavity. The solvent was water or water.methanol mixtures. The 4 mm diameter of the sphere is significant relative to the wavelength of the X-band microwaves (33 mm at 9.1 GHz). The high dielectric constant of the solvent results in a microwave phase shift and distortion of the CW EPR signal for the sample surrounded by the solvent. When water was used, the phase shift of the EPR signal was about 180°. Three computational approaches were used to calculate the microwave phase shift: quasi-static, plane-wave superposition, and finite elements. The three methods were in good agreement with each other and with the experimental phase shifts.

204 IN VIVO DETECTION OF DRUG RELEASING PROCESSES IN IMPLANTED POLYMERS BY LOW FREQUENCY EPR SPECTROSCOPY. **Karsten Mader, Bernard Gallez, Jim Liu, and Harold M. Swartz. Dartmouth Medical School, Hanover, NH 03755**

Although the implantation of polymers is used widely clinically to get a sustained release of drugs, the mechanism of this release, specially under *in vivo* conditions, is not fully understood. Polymers of different types (Eudragit RS, polyhydroxybutyric acid), doped with salicylic acid or sodium salicylate, were loaded with pH-sensitive nitroxides. The EPR spectra of nitroxides in the solid implants typically reflect immobilization and these spectra change to freely rotating when the nitroxides are released spontaneously and/or as the polymer degrades. The hyperfine splitting constant of this free component depends on the pH of the medium in the microenvironment. The release of nitroxides from these implants was followed in vivo after subcutaneous implantation of the polymer foils in the backs of mice. The EPR spectra were recorded on a home made low frequency (1.1 GHz) spectrometer using a surface-coil. Our results indicate that the kinetics of release (mobilization of the nitroxides) as well as the pH inside the implants are governed both by the properties of the polymers and by the drug added to the polymer. The rate of bioreduction of the nitroxide (1 hour to 15 days) also depended on the rate of degradation of the implant.

205 ENZYMIC ACTIVITY OF GLYCERALDEHYDE-3-PHOSPHATE DEHYDROGENASE IS CORRELATED WITH THE NUMBER OF ACTIVE CENTERS UTILIZED WITHIN THE TETRAMER
Joachim. Baumann (a), Reinhard Hensel (b), Pia D. Vogel (a), and Wolfgang E. Trammer(a),
a) Fachbereich Chemie Universitat Kaiserslautern and
b) Tnstitut fur Mikrobiologie, Universitat Essen, Germany

Glyceraldehyde-3-phosphate dehydrogenase (GAPDH) from most sources is an NAD-dependent tetramer with high cooperativity in coenzyme binding. The active sites are related by twofold symmetry with two adenine moieties each being in close vicinity. NAD derivatives spin-labeled at the adenine ring in complex with GAPDH show complex ESR spectra due to dipolar splitting between adjacent radicals. We have shown previously that the enzymic activity of GAPDH from rabbit muscle is correlated with the utilization of some or all the active^sites within the tetramer as revealed by the degree of dipolar splitting. Highly active enzyme is very unstable whereas commercial preparations of lower activity are stable but with two functioning sites, only. Here we describe corresponding studies with GAPDH from various bacterial sources which are known to exhibit lower but stable activities.

206 THE IONIZED A-CENTRE AND OTHER DI-NITROGEN DEFECTS IN DIAMOND. **Qwain D. Tnrkpr, Mark E. Newton, and J. Michael Baker, Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford, OX1 3PU, UK.**

^{14}N ENDOR and ^{13}C EPR measurements have been performed on the optically excited W24 defect in diamond. We believe that these are the first ENDOR measurements on any optically excited defect in diamond. Optical/EPR measurements have also been made to study the excitation energy threshold and lifetime of the W24 centre. Interpretation of the results shows beyond reasonable doubt that W24 is indeed the singly ionized A-centre ($[N—N]^+$): the A-centre optical centre in diamond. The reasons for the creation of the $[N—N]^+$ centre are considered, together with the possible occurrence of $[N—N]^+$ without optical excitation. The geometry of the PI and $[N—N]^+$ defects is predicted from the hyperfine parameters, and it is shown that the results are consistent with the models for the two defects and the results of recent ab initio calculations. We show that the ^{14}N quadrupole interactions for several different centres in diamond, are consistent with a simple theoretical model and compare the $[N-N]^+$ centre with the W7($[N-C-C-N^+]$), N4 ($[N-C-C-N]^+$), and Nl ($[N-C-N^+]$) centres, also observed by EPR and ENDOR.

207 EPR STUDIES OF RADICALS IN ZEOLITES

Gregory L. Turner, Patrick M. Brown, U.S. Bureau of Mines, Tuscaloosa Research Center, Tuscaloosa, Al. 35486 and Martin G. Bakker The Chemistry Department, The University of Alabama Tuscaloosa, Al 35487-0336

The Bureau of Mines has developed a process for containment of high level arsenic bearing waste using a zeolite-cement matrix. The unusually high arsenic loading levels warrant a study of the mechanisms of containment, particularly determination of the site at which the arsenic binds. However, it is difficult to determine the binding site by the methods which are currently available. Therefore, to get at this problem it is necessary to use the known sensitivity of EPR labels to chemical environment in zeolites. It is also necessary to determine the variations in the EPR spectra, with zeolite type, loading of water and the presence of cementitious materials.

The cavity of zeolites X and Y is sufficiently large that molecules the size of the spin probe 4-amino-TEMPO can readily be accommodated and adsorption from cyclohexane by these zeolites has been observed. On absorption the rotational and translational mobility of the spin labels decrease substantially. This results in severely broadened EPR spectra. Because adsorption into the zeolite raises the effective local concentration the spectra generally show considerable line broadening due to spin-exchange and/or dipolar broadening. The other approach being used is to use the Cu^{2+} present in the arsenate waste EPR signal as a probe of arsenate binding

208 EPR-EVIDENCE OF NO-FORMATION IN ANIMALS ORGANS UNDER GAMMA-IRRADIATION.

Nina V.Voevodskaya, Anatoly F.Vanin. Institute of Chemical Physics Russian Academy of Science, Kosygin st.4 Moscow 117977 Russia

It is generally accepted that nitric oxide which is synthesized from L-arginin by NO-synthase accounts for diverse biological effects. A modulation of the activity of this enzyme may essentially alter metabolical and physiologikal processes through the organism-^ It was tasted the effect of gamma-irradiation on NO synthesis in mice.The resalts demonstrate that gamma-irradiation on animals may lead to a potentiation of NO-synthesis in their tissues. The method employed to determine the rate of N0-synthesis was the TPR-spectroscopy registration of the increase in intencity of the signal due to trapping of NO into mononitrosyl iron complexes with diethyldithiocarbamate injected intraperitonally. Using the inhibitor of protein synthesis, cyclohexiimid, it was shown that gamma-irradiation as well as biological cytokinins and iron ions does not activate the constitutional NO-synthase but causes the synthesis of the inducible NO-synthase which begins the nitric oxide generation.

209 UTILIZING ELECTRON PARAMAGNETIC RESONANCE OF THE P_b CENTER AS A PROBE OF INTERFACIAL STRESS IN Si/SiO_2 SYSTEMS. **J. T. Yount. P. M. Lenahan. The Pennsylvania State University, University Park, PA 16802.**

We have utilized electron paramagnetic resonance of Pb centers at (111) Si/Si02 interfaces as an indicator of interfacial stress. Changes in the interfacial stress alter the backbond angles of the Pb defect, and thus the gi component of the defect's g-tensor. As an illustration of this method, thermal nitridation of Si02 in NH3 introduces a near-interface nitrogen-rich region and we find that, consistent with stress measurements (H.S. Momose, T. Morimoto, K. Yamabe, & H. Iwai, IEEE IEDM Tech. Dig. 1990. 65), this decreases the compressive interfacial stress and increases the p-character of the Pb center dangling bond. Thermal reoxidation of this nitrided oxide system results in a return of the system's stress and the P_b center's structure to a pre-nitridation state.

(This work was supported by the Office of Naval Research.)

210 AN ESEEM STUDY OF ^{14}N COUPLING IN VANADYL PHTHALOCYANINE. **Chuanfang Zhang and Jack Peisach, Department of Molecular Pharmacology, Albert Einstein College of Medicine,1300 Morris Park Ave., Bronx,NY10461.**

Three-pulse ESEEM studies have been carried out on vanadyl phthalocyanine (VOPc) in H_2SO_4 glass and in doped VOPc in powdered, metal-free phthalocyanine (Pc).The use of tau-suppression techniques and mutifrequency ESEEM measurements have enabled us to make an unambiguous assignment of ESEEM features. Accurate coupling parameters were obtained based on the frequency of the deep ^{14}N modulations found. For the glassy sample, the four directly coordinated nitrogens in the equatorial plane of VOPc are coupled inequivalently with the hyperfine coupling along the orientation perpendicular to the V = 0 axis equal to: 6.6, 6.9, 7.2, and 7.6 MHz. The hyperfine coupling along the V = 0 axis, however, is a single value, 7.8 MHz. For the doped sample, the same type of inequivalence in the perpendicular orientation and equivalence in the parallel orientation is observed. The remote nitrogens in Pc are too weakly coupled to the VO^{++} to contribute any recognizable feature in the ESEEM spectrum. We provide experimental results that indicate that the ESEEM method, in comparison with ENDOR, provides better spectral resolution for the study of superhyperfine coupling of ^{14}N to the metal ion in vanadyl complexes.

211 ANNEALING CHARACTERISTICS OF THE E' AND PEROXY RADICAL HOLE CENTERS IN OXYGEN EXCESS AND OXYGEN DEFICIENT VITREOUS SiO_2* **Lin Zhang, Wm. R. Austin, and Robert G. Leisure, Colorado State University, Fort Collins, CO 80523, USA**

The production of radiation damage in oxygen excess and oxygen deficient silica is investigated by electron paramagnetic resonance (EPR) as the samples undergo a series of x-irradiations and thermal anneals. Two spin active defects, the E' center and peroxy radical hole center, are induced by the irradiation. For the oxygen excess samples, after an initial irradiation, the E' centers can be removed completely by a soft anneal (20 min. at 250 °C). However, repeated irradiation/anneal cycles show that the anneal *does not* return the material to its pristine condition. In particular, the peroxy radical hole center signal *increases* with annealing and is partially bleached by the following irradiation. Also, the x-ray dose dependence of the E' signal is altered by such cycles. In contrast to the case for the oxygen excess sample, the E' centers in the oxygen deficient samples are not removed by a soft anneal.
•Research supported by Office of Naval Research; Contract No. N00014-91-J-1607 (G.B. Wright)

212 MATRIX PEAK SUPPRESSION IN ^{1}H ENDOR OF PARAMAGNETIC IONS IN DISORDERED SOLIDS: DISTANCE - DEPENDENT ENHANCED ENDOR PHASE (DEEP) SPECTROSCOPY **Ming Zheng and G. C. Dismukes, Princeton University, Department of Chemistry, Hoyt Laboratory, Princetion, New Jersey, 08544**

It is well known that in many cases the most dominant peak in *H ENDOR spectra of paramagnetic ions in disordered solid is the so called matrix peak, arising from distant protons. We have found that the CW proton ENDOR phase response is a function the distance of separation between the proton and the paramagnetic center in aquo Mn(II), Gd(IT), Cu(II) and [Mn(ffl)Mn(IV)02](Bipy)4^{3+} systems. This observation enables a new method termed Distance-dependent Enhanced ENDOR Phase (DEEP) spectroscopy for enhancing spectral resolution and suppressing the matrix peak. When DEEP spectroscopy is applied to the solvent protons surrounding Mn(II) ions, a four-fold increase in spectral resolution is achieved. This enables resolution of two distinct hyperfine couplings from distinguishable groups of molecules in the second solvation shell at 4.3 A and 5.0 A, as was previously predicted by molecular dynamics simulation (Sivaraja et al, /. *Am. Chem. Soc.* 1992,*114*,9600 - 9603.). DEEP spectroscopy has enabled resolution, for the first time, of the weak hyperfine coupling (0.21 MHz) to protons at 7.5 A in the third solvation shell, also as previously predicted by molecular dynamics simulation. DEEP spectroscopy holds promise for studies of solvation to many paramagnetic ions, including those used as MRI contrast agents. Supported by the NIH grant GM 39932.

413 PULSED EPR STUDIES OF A NEW SODIDE, Cs+(21C7)Na-. **Kerry A. Reidv-Cedergren. James L. Dye and John L. McCracken, Department of Chemistry and Center for Fundamental Materials Research. Michigan State University, East Lansing, Michigan, 48824.**

Alkalides are compounds in which an alkali metal serves both as the cation and the anion. It is assumed that electron trapping occurs at the anionic site as was evidenced by cw-EPR, cw-ENDOR and ESEEM experiments. The system of interest in this study is a new alkalide, Cs^{+}(21C7)Na-, in which a Cs+ occupies the cavity of a 21C7 molecule and occasionally, trapped electrons occupy the Na" site. ESEEM techniques were used to measure the weak, superhyperfine couplings between the trapped electron and nearby magnetically coupled nuclei, which then allows one to understand better how the unpaired electron spin density is delocalized in the molecular framework. The ESEEM results have shown the presence of Cs cations which can be directly related to Cs^{+}-Na" distances, therefore confirming the presumed location of the trapped electrons. **This research was supported by NSF Solid State Chemistry Grant No. 90-24525 and by the MSU Center for Fundamental Materials Research.**

414 SELECTIVE INHIBITION OF LIPID PEROXIDATION BY PBN IN RAT LIVER MICROSOMES. **Hong Sang. Yashige Kotake, Coit M. DuBose and Edward G. Janzen, National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, 825 N.E. 13th Street, Oklahoma City, Oklahoma 73104, USA.**

It has been known for some time that spin adducts of PBN are formed when rat liver microsomal dispersions are subjected to lipid peroxidation conditions. Also, the malondialdehyde (MDA) test for lipid peroxidation products shows inhibition by PBN in a dose dependent manner. Now we are able to show by mass spectrscopy that only certain lipids with unsaturated fatty acid chains are removed by lipid peroxidation initiated by various initiators, and PBN prevents the disappearance of this component in a dose dependent manner. The data from EPR spin trapping, MDA testing and MS analysis will be compared in this study. For example, from carbon tetrachloride/NADPH initiated lipid peroxidation in the presence of PBN, the trichloromethyl radical spin adduct is detected, MDA production is quenched and the disappearance of arachadonate is prevented in a dose dependent manner. Results will be presented along with a description of the MS techniques.

415 ANISOTROPY RESOLVED EPR, **Gustavo A. Sierra. Arthur Schweiger, and Richard R. Ernst, Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland**

A two-dimensional pulsed EPR technique for disordered systems based on the standard three pulse stimulated echo sequence and a rotation of the sample or a magnetic field jump perpendicular to the static field is presented. The preparation period consisting of the first two rc/2-pulses creates an oscillating polarization pattern in the inhomogeneously broadened EPR line. In the normal three pulse echo sequence the third 7t/2-pulse creates an FID consisting of the Fourier transform of the polarization pattern, e.g. the stimulated echo. When the orientation of an anisotropic sample is changed after the preparation period the phase of the polarization pattern will change depending on the degree of aniosotropy and the rotation angle. The resulting echo will be shifted in phase. By varying the degree of the reorientation angle while recording the echo intensity an echo oscillation can be measured. After Fourier transformation the different anisotropic components show different frequencies characteristic for the gradient of the resonance tensor at the specific static field value B_0. By recording these anisotropic spectra for different B_D values the usual B_0-field spectrum can be spread into a second dimension representing the anisotropy of the system. Prospects of the method, simulations and first experimental results will be presented.

lb ELECTRON ZEEMAN RESOLVED EPR, **Gustavo A. Sierra. Arthur Schweiger, and Richard R. Ernst, Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland**

A method is presented, which allows to disentangle overlapping spectra into a second dimension according to the differences in their g-values. Depending on the requirements with respect to time or resolution different pulse schemes are possible. A first scheme is based on the standard stimulated echo sequence. The preparation period, consisting of a :c/2-T-7t/2 pulse sequence, creates an oscillating polarization pattern in the inhomogeneously broadened EPR line. A subsequent magnetic field jump AB_0 in z-direction changes the phase of this pattern resulting in a phase shift of the echo. Recording the echo intensity at time *x* after the third *n/2* pulse as a function of AB_0 results in an echo oscillation. After Fourier transformation a g-value spectrum is obtained. The same oscillation pattern can be measured with the hole burning sequence. Here the hole burnt by the initial selective rc-pulse is transformed by the subsequent AB_0 field jump. A nonselective u/2-pulse recalls the new hole pattern consisting of one hole per g-value. The spectrum obtained by Fourier transformation of the observed FID contains the characteristic frequencies for the involved g-values. By recording these electron Zeeman resolved spectra for different B_Q the usual field swept spectra are spread into an additional g-dimension. Prospects of the method, simulations and first experimental results will be presented.

417 **RATES OF NITRIC OXIDE GENERATION FROM ACTIVATED MURINE MACROPHAGES DETERMINED BY SPINTRAPPING** **Toru Tanigawa. Mari Tanigawa, Ikuko Ueno, Yashige Kotake, and Edward G. Janzen, The National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, Oklahoma City, OK73104.**

A real time monitoring system for nitric oxide from macrophages was designed using spin trapping. *N*-Methylglucaminedithiocarbamate (MGD) combined with Fe^{2+} ion in buffer was used as a spin trap. In the culture media, RPMI, under aerobic conditions, ferrous iron in the spin trap was stable for hours. The adduct, MGD_2-Fe^{2+}-NO, was EPR detectable for hours. Thioglycolate-elicited mouse peritoneal macrophages were settled in FCS treated EPR flat cuvettes, and stimulated with LPS and mouse recombinant y-interferon for 3 h. Subsequently, fresh RPMI was continuously injected through the cuvettes during incubation. A solution of the trap in RPMI was introduced into a cuvette containing macrophages. A three line EPR signal of the adduct was continuously monitored. The growth of the signal was fast for several minutes, and then slowed. The rate of adduct formation in the early phase was comparable with that measured by the Greiss reaction assay. (RPMI = Rosewell Park Memorial Institute media; FCS = fetal culf serum; LPS = lipopolisaccharide)

418 **HYDROPHOBICITY PROFILES ACROSS PHOSPHOLIPID BILAYER MEMBRANES AT THE INTERFACE OF GRAMICIDIN AND LIPID.** A. Wisniewska[1,2], J.S. Hyde[2], A. Kusumi[3], and W.K. Subczynski[1,2]. institute of Molecular Biology, Jagiellonian University, Krakow, Poland, [2]National Biomedical ESR Center, Milwaukee, WI 53226, USA, [3]Dept. of Pure and Applied Sciences, Tokyo University, Tokyo, Japan.

The hydrophobicity profiles across phosphatidylcholine (PC) membranes containing various amounts of gramicidin have been examined by using nitroxide spin probes attached to stearic acid (n-SASL) and the headgroup of PC (Tempo-PC). The z - component of the hyperfine tensor A_z obtained from the X-band ESR spectrum of the frozen suspension of PC membranes has been used to monitor hydrophobicity of the environment around the nitroxide moiety. Incorporation of gramicidin (15 mol%) to the membrane containing either saturated or unsaturated lipids significantly decreases hydrophobicity (increases polarity) of the central region of both bilayers, but does not change the water accessibility to the polar headgroup region. After addition of gramicidin, the shapes of the hydrophobic barrier in saturated and unsaturated membranes become very similar even though they differ significantly in its absence. The results were further confirmed in the fluid phase membranes by observing the rate of collision of $Fe(CN)_6^{3-}$ or Ni^{2+} with the spin probe in the membrane using continuous wave saturation ESR measurements.

419 OXYGEN TRANSPORT WITHIN AND ACROSS THYLAKOID MEMBRANES OF SPINACH CHLOROPLASTS. A. Ligeza[1-2], J.S. Hyde[2], and W.K. Subczynski[1,2]. institute of Molecular Biology, Jagiellonian University, Krakow, Poland, [2]National Biomedical ESR Center, Milwaukee, WI 53226, USA.

Oxygen transport in the thylakoid membranes prepared from spinach leaves has been studied by observing the collision of molecular oxygen with nitroxide radical spin labels placed in the lipid bilayer portion of the membrane at various distances from the membrane surface using electron spin resonance (ESR) technique. The collision rate was estimated for 5-, 9-, 12-, and 16-doxylstearic acids from the linewidths of the spin label ESR spectra measured in the procence and absence of molecular oxygen. The profile of the local oxygen transport parameters across the membrane were obtained showing that the oxygen diffusion-concentration product is higher than in water for all locations at 23°C. From the oxygen transport parameter profile, the membrane oxygen permeability coefficient was estimated according to the procedure developed earlier by Subczynski et al. (W.K. Subczynski, J.S. Hyde, and A. Kusumi, (1989) Proc. Natl. Acad. Sci. USA 86, 4474-4478). At 23°C, the oxygen permeability coefficient for the thylakoid membrane was found to be about two times higher than for the water layer of the same thickness as the membrane.

213 MULTIQUANTUM EPR SPECTROSCOPY WITH TETRACHROMATIC IRRADIATION. W

Froncisz*, M. Jeleii, J. Koziol, and T. Oles". Institute Molecular Biology, Jagiellonian University, Karkow, Poland, and biophysics Research Institute, Medical College of Wisconsin, Milwaukee, 53226

Irradiation of the 1/2 spin system with four microwave frequencies induces many multiquantum transitions. Their intensities and phases depend on the frequency separation of the incident microwaves and the relaxation properties of the spin system. Tetrachromatic microwave irradiation can be realized easily by combining two pairs of microwave frequencies separately generated by two mixers. Their frequencies are *(j>,=u₀±Au/2* **and** *<»2˜u₀±(Ao}/2 +8u>)* **for the first and second pair, respectively. There are 12 different transitions involving the same number of quanta. For three quantum (3Q) transitions, two transitions, appearing at $w_0 \pm 3Aw/2$ and $w_0 \pm (3Aw/2 + 3ow)$, are generated by mixing two incident frequencies originating within one pair, similar to bichromatic irradiation. Another eight 3Q transitions are the product of mixing one frequency coming from one pair and the second from another pair. The so-called "close" 3Q transitions occur at $w_0 \pm (Au/2 - Sw)$ and $w_0 \pm (Aw/2 + 25w)$. The "far" 3Q transitions have frequencies $w_0 \pm (3Aw/2 + 28u)$ and $w_0 \pm (3Aw/2 + 5a))$. Lines associated with higher number of quanta are narrower similar to bichromatic irradiation. The amplitude of the 3Q transitions induced by a weak tetrchromatic field are proportional to T_2 when Aw and $5w < 1/T_x$ and $1/T_2$. For larger Aw and 5w, the amplitudes of "close" and "far" 3Q transitions are sensitive to T_2 and $T_{1?}$ respectively.**

214 NOISE CONSIDERATIONS WITH CRYOGENIC MICROWAVE AMPLIFIERS AND Q-SPOILING. **James S. Hyde^. Susanne Pfenninger, and Wojciech Froncisz, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, 53226**

Use of a cryogenic microwave preamplifier with a noise figure of 0.5 dB (35 K equivalent noise temperature) increases the sensitivity of the system to other noise sources. Losses in the room temperature bridge itself have been determined quantitatively: the equivalent noise temperature of the receiver increases from 35 to 100 K. Overcoupling, a method of Q-spoiling frequently employed in pulse ESR, introduces a source of noise not previously considered in the ESR literature: noise from the equivalent 50 Q room temperature resistor at Port 1 of the circulator contributes to a significant degree. Comparing overcoupling with the method of Q spoiling by introduction of a lossy element, it is shown that the ratio of signal intensities varies between 1 and $2^{1/2}$, favoring overcoupling. However, because of noise contributions from the equivalent 50 0 resistor, the signal-to noise ratio favors lossy-element Q-spoiling when using a cryogenic amplifier. A method to vary the Q of a loop-gap resonator electronically using a GaAs diode is described. It is suggested that automatic computer-based control of the resonator Q and resonator match, use of a cryogenic low-noise microwave amplifier, and cooling of components of the bridge will result in a spectrometer system with ultimate sensitivity.

215 SPIN-LATTICE RELAXATION IN GLASSES. **Jacques Pescia[a]. Sushil K. Misra[0], Guy Ablart[3], Paul Zinson[a] and Delphine Vergnoux[a], a) Laboratoire de Magnetisme et dElectronique Quantique, Universite Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France, b) Department of Physics, Concordia University, 1455 de Maisonneuve Blvd. W., Montreal, Quebec H3G 1M8 Canada**

In order to better understand spin-latice relaxation process in amorphous materials, not well-explained so far, borate glasses doped with Fe203, described by the formula (l-x)B2O3.0.6Li2O3-xFe2O3 with x = 0.0025, 0.005, 0.01, 0.03 have been investigated. The relaxation rate *(1/T\)* was measured over the wide temperature range 5-290K with the use of an amplitude-modulated microwave field, detecting an EPR signal proportional to dM_z/dt by means of a pick-up coil coaxial with the external magnetic field. This method is particularly well-suited to measure short relaxation times (10^{-} J"s<Ti<10-^{6}s). In the sample with x = 0.0025 1/Ti was found to vary with temperature (T) as T^{2} and as T at low and intermediate temperature ranges, respectively. For T>200K, Tj was independent of temperature. For samples with increasing values of x the variations in the relaxation times were of the same form; however, in more concentrated salts the temperatures above which 1/Tj is independent of temperature were lower. These data can be well-explained by the existence of relaxation process effected by exchange pairs, even for x as low as 0.0025. The presence of pairs is confirmed by the appearance of a weak EPR line at g = 2.

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High Frequency (139.5 GHz) Pulsed EPR

Gary J. Gerfen.[1] Lino R. Becerra,[1] Brendan F. Bellew,[1] Souheil J. Inati,[1] Dennis A. Hall,[1] Robert G. Griffin,[1] David J. Singel.[2]

Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139.

•^Department of Chemistry, Harvard University, Cambridge, MA 02138.

Pulsed EPR spectroscopy has been implemented in a spectrometer operating at an electron spin excitation frequency of 139.5 GHz, static magnetic field strength of 5 Tesla. One of two sources is used to generate the microwaves: a phase-locked Gunn diode which produces ~15mW, or a cyclotron resonance maser (gyrotron) which produces up to 100 W. These sources, along with other instrumental details such as switches and resonators, are discussed. Experimental results obtained at 139.5 GHz to be presented include: 1) the measurement of relaxation times of the free radical BDPA doped into polystyrene together with a discussion of their influence on Dynamic Nuclear Polarization (DNP) solid state NMR experiments; 2) the field and orientation dependence of electron spin echo envelope modulation (ESEEM) in nitroxide systems; 3) echo detected EPR spectra of several systems; 4) pulsed ENDOR data.

217 DEVELOPMENT OF HIGH FREQUENCY ESR AT THE NATIONAL HIGH MAGNETIC FIELD LABORATORY

Louis C. Brunei

National High Magnetic Field Laboratory
Honda State University, 1800 E. Paul Dirac Dr., Tallahassee, FL 32306-4005

We will first discuss the potential of very high field ESR spectroscopy in the 250 to 500GHz range. We then present the current development of a high field \ high frequency ESR spectrometer at the National High Magnetic Field Laboratory and the possible use of this spectrometer in the fields of Physics, Chemistry and Biology.

"" VERY-HIGH-FIELD EPR AND THERMAL SPIN POLARIZATION EFFECTS.

Ya. S. Lebedev, N. N. Semenov, Institute of Chemical Physics, Kosygina 4, 117979 Moscow, Russia.

Until now, most EPR experiments were performed under conditions of almost equal population of electron spin levels because one needed T<0.4 K in order to modify spin polarization at magnetic field B = 3 kG. At 2 mm wave band and B = 50 kG, we only need T<6.5 K so new experiments can be performed at liquid helium temperature. The change in line shape caused by spin polarization is expected to be negligible for S=l/2 centers. However, for S>l/2 it should be significant, and should be dependent on temperature and on the sign of the zero-field splitting. These expectations were confirmed for spectra of ground triplet-state biradicals, radical pairs, and for metal-radical complexes with S=l and S=3/2. Some new effects were detected, which required a reinterpretation of existing models for these paramagnetic species.

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Abstract Not Available

219 INDOOR AIR MONITORING BY FT-IR. **P. Jaakkola, Temet Instruments OY, Asentajankatu 3,00810,HeIsinki, Finland; P. Saarinen and J.Kauppinen, Department of Physics, University of Turku, SF-20500,Turku, Finland; C. T. Chaffin, T. L. Marshall, R. M. Hammaker, and W. G. Fatelev.Aero-Survey. Inc.631 Levee Drive, Manhattan, KS 66502 USA.**

The application of Fourier transform infrared spectroscopy to air monitoring at industrial and superfund sites has been most successful. Many volatile organic compounds (VOCs) can be detected in part-per-billion concentration range over a 100 m path length in the atmosphere. Much success has been enjoyed from " outdoor" monitoring of the atmosphere, but what about "indoor" air quality?. We shall present data on indoor monitoring using two different FT-IR instruments simultaneously.

The first FT-IR instrument is an extractive one that measures the atmosphere in a small area of the room. This instrument collects the indoor atmosphere into a 9-meter heated multipass infrared gas cell. This sampling is comparable to point source monitoring measurements. The measurement is comparable to our atmospheric remote sensing FT-IR experiments except the beam is diverted about the room from the source to the FT-IR instrument. The height of the optical path is certainly a variable. Both FT-IR instruments will simultaneously record the atmospheric absorption, and the results from these different measurements will be compared.

220 INFRARED STUDIES OF PHOTOCHEMICAL EFFECTS IN REACTIONS OF BLACK CARBON. **Abdul R. Chughtai and DwightM. Smith, Department of Chemistry, University of Denver, Denver CO 80208.**

Effects of simulated solar radiation on the reactions of black carbon with such gaseous species as SO?, oxides of nitrogen, and ozone have implications for the role of carbonaceous particulate in the troposphere, as experienced by product distribution, rates and mechanisms. Not only does the radiation induce, and in some cases inhibit, the heterogeneous reactions, but photochemical formation of certain surface species promises to affect both the behavior of the carbon in complex reaction environments and for any catalytic activity.

The wet oxidation of SO_2 in the presence of soot is strongly influenced by the presence of simulated solar radiation, the formation of apparently covalent S-O linkages at the carbon surface being one observable effect which has been explored since its initial reporting. The effect of such radiation on the NO_2-soot reaction at the ppm level, on the other hand, is traced to the photolytic dissociation of NOj. FT-IR examination of reactants and products in these reactions has provided evidence for the mechanistic interpretations. Current data on the ozone (ppm)-soot reaction in air, on the reaction of soot with NC^-SO, mixtures, and on reactions of soot containing trace metals are the principal focus of discussion within the context of earlier results.

POLYSULPHIDE SPECIATION IN ALKALINE SOLUTION BY RAMAN SPECTROSCOPY

Kirk H. Michaelian, Carolyn K. Preston. Jaroslaw Szynkarczuk, Zohra Ali, and Daren Sawkey
Western Research Centre, CANMET, Natural Resources Canada
P.O. Bag 1280, Devon, Alberta, Canada, T0C 1E0

Speciation of polysulphides (S_xS^{2-}, x = 1 - 5) in alkaline solution is important for the understanding of the sulphur production mechanism during H_2S electrolysis, where the presence of HS" induces polysulphide formation from pure sulphur. In this work, different polysulphide species were prepared in solution in the presence of >1 M HS" and studied by Raman spectroscopy. Several bands attributable to polysulphide species were identified in the spectra. The data were analysed numerically using a combination of curve-fitting, smoothing and deconvolution in an attempt to quantify the species present in a series of solutions in which the HS" and OH" concentrations varied over a substantial range. It was found that at least four bands are required in order to account for the features in the observed spectra. The concentration dependence of the intensities of these bands suggests their assignment to particular polysulphide species. Similarly, spectra for electrolysed solutions of H_2S were obtained and the bands attributed to individual polysulphides. A correlation between polysulphide rank and current efficiency was established.

222 **HYDRATION OF PARTICULATE CARBON.** **Abdul R. Chughtai, Michael E. Brooks and Dwight M. Smith, Department of Chemistry, University of Denver, Denver CO 80208.**

The interaction of particulate carbon with an aqueous phase underlies, or at least influences, its tropospheric chemistry, its role in light scattering/absorption in the atmosphere, and its health effects as a major constituent of respirable particles. The results of a systematic study of the hydration of soot, designed to explore the nature of the carbon-aqueous interface, are reported.

FT-IR, augmented by microgravimetry, light scattering and SEM, has revealed a strong effect of the carbon surface structure on water vapor adsorption. Effects of aging, oxidation by a variety of oxidants, and incorporation of minerals and trace metals, on soot particle hydration are described.

223 **THE CHEMISTRY OF OZONE AND SOOT AS REVEALED BY INFRARED SPECTROSCOPY AND ANCILLARY TECHNIQUES.** **Abdul R. Chughtai and Dwight M. Smith . Department of Chemistry, University of Denver, Denver CO 80208**

The rapid reaction of ozone with black carbon, even at ozone concentrations in the ppbv range, produces changes in the carbon surface which may be controlling of the atmospheric concentrations of both. The reactions of ozone with n-hexane soot have been examined extensively in these laboratories in recent years, leading to the observation of a range of products, including surface functionalities which underlie remarkable solubility phenomena, and to rate expressions and mechanisms for these reactions.

Reported now are the results of a comprehensive study of the reaction rates and mechanisms of ozone at low concentrations (ppm) with soot under various conditions including the presence of simulated solar radiation.

Simultaneous spectroscopic and microgravimetric measurements have revealed complex reaction sequences which are partially interpretable from knowledge gained in earlier work. Differences manifested through product distribution, rate equations, and through photochemical effects, have their origin in experimental conditions.

224 **NEAR INFRARED GASOLINE OCTANE PREDICTION IN THE LAB AND IN THE FIELD.** **James E. Tackett, Marathon Oil Company, P. O. Box 269, Littleton, CO 80160.**

On-line prediction of gasoline octane values using a near infrared spectrometer, rather than two on-line engines has advantages in the areas of initial cost, analysis tune, maintenance and precision. However, a significant amount of preliminary work must be done to realize these benefits. This includes data base sample selection, calibration, validation, setting up protocols and training. After installation, it is important to monitor results and take necessary actions to correct any problems that are detected. Each of these tasks will be discussed as well as some factors that must be present for a successful field operation. Our experience over a two year period will be reviewed.

225 **ON-LINE NIR SPECTROSCOPY OF OIL SAND SLURRIES**

Waldemar I. Friesen, Carolyn K. Preston, and John C. Donini
Western Research Centre, CANMET, Natural Resources Canada
P.O. Bag 1280, Devon, Alberta, Canada, TOC 1E0

The development of a reliable on-line method to monitor oil sand slurries is essential to improving process control in oil sand extraction plants. Diffuse reflectance NIR spectroscopy has been investigated in a pilot plant environment using an in-line fibre-optic probe. Spectra of a feed slurry were acquired continuously for several hours while oil sand ore type and slurry water content were varied. It is demonstrated by means of principal component analysis that the spectra cluster according to ore type and water content, allowing deviations from and transitions between steady-state conditions of the process to be observed. Estimates are made of characteristic times for the process to reach a steady state after a change in condition is initiated. Classification of the spectra by artificial neural networks on the basis of ore type is also discussed. Primary analytical determinations of oil, solids, and water contents were made by the Dean-Stark method for slurry samples collected at regular intervals during the run. Multivariate calibrations of the spectra were obtained using several techniques, including principal component regression, partial least squares, and neural networks. Using subsets of the data, prediction errors for the constituent concentrations are less than 0.3, 2, and 2 wt% absolute for oil, solids, and water, respectively. Hence, quantitative analysis of an on-line spectrum should be preceded by a classification step to permit selection of the appropriate calibration model.

226 A NEURAL NETWORK FOR FT-RAMAN SPECTRAL INTERPRETATION: ROBUSTNESS. S; Medlin, J. Morris, and R. Fifer, U. S. Army Research Laboratory, AMSRL-WT-PC, Aberdeen Proving Ground, MD 21005-5066

The process of correlating Raman shifts to the presence of different functional groups can be complex and time-consuming. This paper discusses the development of a neural network that assists in FT-Raman spectral interpretation. The topography of the neural network consists of 651 input neurons and a number of hidden-layer neurons. Each input neuron is associated with a specific 4 wavenumber window of the digitized FT-Raman spectra (from 400 to 3000 cm^{-1}). The network is trained to recognize over 260 different functional groups. The neural network has demonstrated the ability to recognize spectra that have very low S/N ratios. This feature allows the network to assist in the interpretation of both complex, rich spectra and also of spectra that have been degraded by instrumental factors such as digitization error or low sampling rates. The robustness of the network has been demonstrated by artificially causing spectra dropouts and distortion of peak shapes. Validation studies are presented that show the ability of the neural network to provide structural information based on both ideal and distorted FT-Raman data.

227 **COMPUTER UPGRADE OF FTIR SPECTROMETER.** **Robert T. Lynch, Abdul R. Chughtai, and Dwight M. Smith. University of Denver, 2050 E. Iliff Ave, Denver CO 80208. (303) 871-2616.**

Fourier transform based spectrometer instruments are comprised of two main components, the spectrometer and its controlling computer. The rapid advancement of the computer industry over the past fifteen years has made the controlling component of an otherwise adequate spectrometer obsolete. An alternative to replacing the entire spectrometer (a somewhat costly option) is to upgrade the computer system to today's technology. There are many advantages to upgrading. 1) The speed of the fourier transform process is significantly higher. 2) It is very easy to repair and/or replace the controlling computer if and when it breaks down. 3) The software provides greater feedback of the system status. Standard off-the-shelf analog-to-digital converters and digital I/O units are used which plug directly into the bus of a 486 computer. The computer performs many tasks. 1) Initialization of the spectrometer to operate in the desired mode. 2) Monitoring of error conditions. 3) Conversion of analog spectrometer data into digital form. 4) Performing FFT conversion. 5) Conversion to absorbance and/or transmittance form. 5) Generating ASCII data files which allows transfer of data to various other software packages.

228 CHOOSING THE PROPER INTERNAL REFLECTION ACCESSORY FOR YOUR SAMPLE. W. D. Perkins, The Perkin Elmer Corporation, 2305 Bering Drive, San Jose, CA 95131

Internal reflection has been used in infrared spectroscopy since the early 1960 s. Over the intervening years sampling accessories for internal reflection have undergone many refinements and taken on a number of new configurationso They are now used as routinely for liquid samples as for solid samples. This paper will survey the multitude of accessories now in common use and will discuss them in terms of their applicability for various types of samples.

229 **CONSEQUENCES OF THERMAL DIFFUSION LENGTH IN THE FTIR/ PHOTOTHERMAL SPECTROSCOPY.** **T. Mahmood. and J.R. Schlup, Department of Chemical Engineering, Durland Hall, Kansas State University, Manhattan, KS 66506-5102.**

The "mirage effect" in photofhermal spectroscopy is the deflection of a probe beam by refractive index (n) gradients in a fluid above a surface heated by a modulated pump beam. The mirage effect in the "reverse " geometry can be advantageous over the "normal" geometry since, with proper alignment, the deflecting medium makes no contribution to the photofhermal beam deflection (PBD) signal. The magnitude of probe beam deflection is greatly dependent-on the thermal properties of the sample and the deflecting medium. In particular, the relationship between the thermal diffusion length, position of the focus of the pump beam, and the sample size is a key factor in interpreting FTIR/PBD spectra. The impact of the thermal diffusion length on the sample geometry and instrument configuration of photofhermal spectroscopy experiments will be demonstrated using data from a variety of polymer samples.

230 **A FEASIBILITY STUDY OF NIR SPECTROSCOPY FOR DETERMINATION OF AROMATIC AND DISTILLATE PROPERTIES IN DIESEL AND JET FUELS**
Carolyn K. Preston, S. Win Lee, Elaina F. Olsen, and Waldemar I. Friesen
Western Research Centre, CANMET, Natural Resources Canada
P.O. Bag 1280, Devon, Alberta, Canada, TOC 1E0

A set of 40 diesel and jet A fuels was studied to ascertain the correlation between NIR response and middle distillate properties. The sample properties measured included: hydrogen, nitrogen and sulphur contents; aromatics content by SFC and FIA; distillation range by ASTM D2887 and D86; aniline point; cetane index; cetane number; cloud point (diesel); and freezing point (jet). The NIR spectra of the samples were measured in the region 1100-2500 nm on two different NIRSystems 6500 instruments. Although the diesel and jet fuel spectra were very similar as demonstrated by a principal component analysis, the differences were sufficient to warrant separate calibrations based on fuel type. In general, the NIR calibrations by multivariate linear regression and partial least-squares for the properties of the diesel fuel were better than those for the jet fuel. Most calculations using spectra yielded excellent or at least acceptable results when compared with the ASTM reproducibility limits. Furthermore, it was found that the calibration equations developed for the cetane index of both the jet and the diesel fuels on one spectrometer could be used for spectra obtained using the other instrument, if suitable bias corrections were made.

231 **MATRIX-ISOLATION OF LASER DESORBED SPECIES UTILIZING A CRYOGENIC TRAP/FT!R INTERFACE.** **Bryan L Carr. Robert S. Brown, Utah State University, Dept. of Chemistry and Biochemistry, Logan, Utah 84322.**

The capability of cryogenic trapping of laser desorbed compounds combined with infrared spectrometry has been previously described.[1] One limitation of this technique is the lack of adequate sensitivity needed to detect low levels of laser induced degradation products. This lack of sensitivty and/or spectral quality can be attributed to bandbroadening caused by intermolecular interaction and, to a lesser degree, rotational transitions. Matrix isolation minimizes bandbroadening by separation of individual molecules in a "cage-like" structure of inert gas. The feasibilty of matrix isolation of laser ablated material has been demonstrated using a cryogenic trap/FTIR interface. Experimental parameters such as laser power, sample introduction and matrix gas introduction have been optimized to enhance matrix isolation. The capability of this method for the detection of low level degradation products of matrices used in MALDI mass spectrometry will also be addressed.

1. R.S. Brown and N.L. Gilfrich, Appl. Spect., 44, 8 (1990).

232 SOLID-MATRIX LUMINESCENCE PROPERTIES OF BENZO(A)PYRENE-DNA ADDUCTS AND THEIR HYDROLYSIS PRODUCTS. **R. J. Hurtubise. J. S. Corley, Y. Chu, L. Shu, and S. W. Tjioe, Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071.**

An important step in the chemical carcinogenesis of benzo(a)pyrene [B(a)P] is the covalent binding of B(a)P to DNA. Highly sensitive and selective analytical methods are needed for the characterization and determination of B(a)P-DNA adducts and their hydrolysis products. Several solid materials have proven to be very effective for obtaining room-temperature fluorescence and phosphorescence from B(a)P-DNA adducts and their hydrolysis products. For example, different types of filter paper, cyclodextrin salt mixtures, and trehalose salt mixtures can be employed to obtain solid-matrix luminescence from these species adsorbed at very low levels. A variety of photophysical parameters have been obtained for B(a)P-DNA adducts, a B(a)P-guanosine adduct, and tetrols, which are the hydrolysis products of B(a)P-DNA adducts. These data have helped to elucidate some of the interactions of the adducts and tetrols with the solid matrices. In addition, several ways of characterizing and quantitating these components have emerged. A number of the important results from these studies will be presented.

233 FLUORESCENCE ENERGY TRANSFER MEASUREMENTS OF RH0D0PSIN PH0T0STATES TRAPPED IN TREHALOSE FILMS. **Sharon Sikora and T. Gregory Dewey, Department of Chemistry, University of Denver, Denver, CO 80208***

The mammalian photoreceptor, rhodopsin, shows a complex series of thermal transitions after light activation. By suspending rhodopsin in trehalose-water glass films, it is possible to trap photostates in this light-activation process. Because of the unusually high vitrification temperature of trehalose-water, this trapping can be accomplished at room temperature. This allows for a facile investigation of the spectroscopic properties of the photostates of rhodopsin. Depending on experimental conditions, it is possible to trap two different photointermediates, metarhodopsin I and metarhodopsin II. Fluorescence energy transfer has been measured from extrinsic probes located at specific amino acid residues on the rhodopsin to the chromophore, retinal. Distances between these locations were calculated from these measurements. It is seen that these distances are the same for rhodopsin and metarhodopsin I while metarhodopsin II shows a considerable difference. The present results suggest that large structural changes have occurred in the transition to metarhodopsin II.

234 SOLID-PHASE EXTRACTION AND SOLID-MATRIX LUMINESCENCE AS AN ANALYTICAL TOOL. **Jie Chen and Robert J. Hurtubise, University of Wyoming, Department of Chemistry, Laramie, Wyoming, 82071-3838.**

A solid-phase extraction (SPE) technique with Whatman IPS paper, which is coated with silicone and contains a tin complex, was investigated as an alternative method for the isolation of organic compounds from aqueous solution. This separation approach was combined with solid-matrix room-temperature fluorescence (RTF) and room-temperature phosphorescence(RTP). The primary advantages of the SPE-RTF-RTP methodology are its simplicity, speed, and potential to be developed into a field-testing method. Another major advantage is that with the IPS paper RTP can be obtained from adsorbed polycyclic aromatic hydrocarbons without a heavy atom adsorbed on the solid matrix. Phenanthrene, benzo(a)pyrene, benzo(f)quinonne, and tetrol 1-1, which is a hydrolysis product from benzo(a)pyrene-DNA adducts, were studied as model compounds. It was found that these compounds could be readily absorbed onto IPS paper from water solutions, and that the RTF and RTP intensities of the adsorbed compounds were proportional to the amount of compound in the aqueous solutions. The linear dynamic ranges, the limits of detection, and the standard deviations of the new technique were obtained. Several analytical aspects of the SPE-RTF-RTP approach will be considered.

235 APPROACHES TOWARDS HIGH-SPEED DNA SEQUENCING BY USING CAPILLARY ELECTROPHORESIS. **Edward S. Yeung. John A. Taylor, Kyoji Ueno, Xiandan Lu, and Qingbo Li, Department of Chemistry and Ames Laboratory. USDOE, Iowa State University, Ames, Iowa 50011.**

A fluorescence detector for capillary electrophoresis with the ability to simultaneously monitor separations in multiple capillaries in real time is described. This multiplexing approach involves laser illumination of a bundle of optical fibers which are inserted into a capillary array. Alternatively, the laser is focused into a line for excitation. The array is imaged orthogonally through a microscope onto a charge-coupled device camera for signal analysis. The technique is demonstrated for one hundred capillaries and considerations for upscaling to as many as four thousand capillaries are discussed. This will greatly speed up the sequencing step in DNA analysis.

236 FLUORESCENCE STUDIES OF SURFACE BINDING, HETEROGENEITY, AND MIGRATION OF SILOXANE LIGANDS ON SILICA, H. Wang and J. M. Harris, Department of Chemistry, University of Utah, Salt Lake City, UT 841*12.

Covalent attachment of ligands by siloxane bonds to silica surfaces is routinely employed in the synthesis of chromatographic stationary phases, the immobilization of reagents, and the control of surface properties. The performance of these materials depends on the organization of the bound ligands and how the binding chemistry is affected by local surface environment. In this talk, time-resolved spectroscopic studies of a fluorescent siloxane ligand (3-(l-pyrenyl)-propyl-dimethylchlorosi* lane (3PPS)) bound to silica is used to characterize the distribution of molecules on the surface and observe their encounters through excimer emission. From these studies, we report the migration of covalently-bound siloxane species on silica surfaces. The slow time-scale migration of siloxane ligands also coincides with changes in the heterogeneity of surface environments as determined by the distribution of fluorescence decay rates of the isolated probe molecules. Significant differences in the emission behavior of chlorosilane and hydroxys!lane reagent is observed that can be attributed to differences reactivity with populations of silanols on the silica surface. The impact of this surface chemistry on the stability of reversed-phase chromatographic materials will be considered.

237 LUMINESCENCE BASED OXYGEN SENSORS, **J. N. Demas and Wenying Xu, Department of Chemistry, University of Virginia, Charlottesville, VA 22901 and B. A. DeGraff, Department of Chemistry, lames Madison University, Harrisonburg, VA 22807**

Luminescence quenching by oxygen is an extremely attractive method of analyzing O2. While organic molecules have long been tested as sensors, platinum metal complexes (e.g. Ru, Os, Ir, Re) show great promise as sensor materials. They have high luminescence efficiencies (0.04-0.8), long lifetimes (0.2-120 us), intense visible absorptions (5,000-30,000), and are robust. These properties make them ideal for low cost intensity and lifetime quenching methods for measuring oxygen concentrations. While the design of metal complex with specific and desired luminescence properties is relatively advanced, the understanding of the role of the support in affecting quenching properties of sensor molecules is still in its infancy. We have systematically studied the effect of polymer structure on sensor properties. [Ru(Ph2phen)3]Cl2 (Ph2phen= 4,7-diphenyl-l,10-phenanthroline) and pyrene have been used as probes in a wide range of dimethylsiloxane containing polymers. Issues addressed include the degree of quenching as a function of polymer and sensor structure, the role of domain structure in controlling response, heterogeneity of response as demonstrated by nonlinear Stern- Volmer plots, and the significance of fillers such as silica. Guidelines for sensor design are presented.

ENVIRONMENTAL ANALYSIS VIA TUNABLE LASER INDUCED FLUORESCENCE SPECTROSCOPY. **Gregory D. Gillispie and Randy W. St. Germain, Department of Chemistry, North Dakota State University, Fargo, ND 58105.**

Applications of a novel field-operable, tunable laser spectrometer system will be presented. Organic contamination in groundwater and soil have been monitored via fluorescence over fiber optic cables up to 100 meters long. Time-resolved detection is integral to the approach. We will illustrate identification of contaminant fuel class by visual and chemometric analysis of two-dimensional wavelength-time matrices. Lasers are better than incoherent sources for launching light into a fiber and a variable wavelength excitation source is likewise desirable. Nonetheless, the *perceived* disadvantages of tunable lasers have severely restricted their field use to date. However, our introduction of a Bethune prism cell into the dye laser oscillator confers a high degree of reliability and convenience. Performance characteristics in the field are comparable to those provided by commercial dye lasers designed strictly for laboratory operation. Detection options include spectrograph/CCD camera or a monochromator, photomultiplier tube, and digital storage oscilloscope combination. The laser source, fiber optic probe, and detector are fully integrated into a compact unit that is easily transported and quickly installed at the site. Specialized control and analysis software allows the unit to be operated by relatively inexperienced personnel.

239 EVALUATION OF FLUORESCENCE EXCITATION-EMISSION MATRICES FOR IDENTIFICATION OF REAL WORLD OIL SPILLS. **Martha S. Hendrick. USCG Marine Safety Laboratories, Groton, Connecticut 06340; James D. Stuart, University of Connecticut, Storrs, Connecticut 06269; Richard B. Gaines, USCG Academy, New London, Connecticut 06320.**

The ASTM standard method for characterizing spilled petroleum oil using fluorescence spectroscopy is based on emission spectra with excitation at a fixed wavelength. Collecting a succession of emission scans and combining the information into an excitation-emission matrix increases spectral information, but can be time consuming. Technological improvements now allow for the collection of the emission spectra, without distortion, within one hour. The data are most easily visualized with contour plots. With excitation and emission slits at 3 nm, scans must be collected at 1 nm intervals to collect sufficient data so die plot does not appear "boxy." For oils released into the environment, the processes of evaporation and biodegradation affect the weathering rates of the components of oil to different degrees. Just as the shape of a single emission scan becomes distorted and is difficult to compare with similar oils, the appearance of the contour plot is also affected by weathering which makes visual comparisons difficult. Data from real spill cases are compared with capillary gas chromatography as a benchmark technique.

240 TOTAL FLUORESCENCE SPECTRAL AND LIFETIME ANALYSIS OF ALUMINUM BINDING BY A COMMERCIAL HUMIC ACID. **Charles M. Sharpless. Linda B. McGown, Duke University, P.M. Gross Chemical Laboratory, P.O. Box 90348, Durham, North Carolina 27708-0348**

Complexation by humic substances is well recognized as an important mechanism affecting the fate of metals in the environment. Of the many techniques used to study such behaviour, fluorescence spectroscopy has proven to be particularly useful. Binding constants between humics and heavy metals have been measured by taking advantage of the fact that metals such as copper and lead quench the intrinsic fluorescence of the humics. While such information is extremely useful, it provides little insight into the effect of metal binding on the molecular conformation of the humics, a property which affects their transport and affinity for other substances (e.g., PAH's). Our group has concentrated on the analysis of humic samples via total luminescence spectral and Ufetime techniques. Recently, we have begun to investigate the effects of a lighter metal, aluminum, on the photophysical properties of a commercially available humic acid. Our studies include absorption and circular dichroism, as well as total luminescence and Ufetime measurements of the intrinsic humic fluorescence. Such measurements should aid in characterizing the conformational changes induced in the humic acid upon binding of aluminum.

241 **TOTAL FLUORESCENCE LIFETIME CHARACTERIZATION OF COMPLEX SAMPLES.** **Sherry L. Hemmingsen. Jeremy M. Shaver, Linda B. McGown, Duke University, P. M. Gross Chemical Laboratory, P. O. Box 90348, Durham, North Carolina 27708-0348.**

The characterization of complex samples is often accomplished by studying isolated fractions of a sample. However, important information can be gained by focusing on the uniqueness of the sample as a whole. In an effort to develop fingerprinting methods for highly heterogeneous samples, our group has used total luminescence and fluorescence lifetime techniques to study coal liquids, human sera, and humic substances. In some cases, total luminescence alone shows promise for distinguishing between samples. Yet, for other samples, the broad spectral peaks of their fluorescence excitation-emission matrices provide only limited detail and discrimination. Fluorescence lifetime information enhances the spectral fingerprinting of complex systems, especially since compounds with similar steady-state fluorescence spectra often have significantly different fluorescence lifetime profiles. Moreover, a multitude of chemical microenvironments can be experienced by fluorophores in such samples, suggesting that distributions in fluorescence lifetimes may exist Total lifetime information can be obtained by collecting lifetimes over a broad spectral bandpass, gready improving signal-to-noise ratios and reproducibility relative to lifetimes at discrete wavelengths. We have used both standard nonlinear-least-squares analysis and the Maximum Entropy Method (MEM) to analyze the total lifetime data for complex samples. In this talk, we will discuss the results for several coal liquids and humic substances, comparing MEM and nonlinear-least-squares methods for the analysis of the total lifetime data.

M* **SOLID-MATRIX LUMINESCENCE FROM TRACE ORGANIC COMPONENTS IN GLASSES PREPARED FROM SUGARS.** **Jiangshan Wang and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071**

A new kind of solid matrix, glasses from sugars, was developed for trace organic analysis. Trehalose/NaCl and glucose glasses were prepared by evaporating sugar solutions onto solid supports at 80-110° C. The solvent used was methanohwater (50:50). It was determined that the ratio of methanol to water was very important in forming a clear glass. Also, glasses made from pure trehalose often cracked. However, by adding 10% NaCl to the trehalose, no cracks were formed. Clear and rigid glasses of both trehalose/NaCl and glucose were obtained on quartz, glass and aluminum plates, and in quartz tubes and in a depression of an aluminum sample holder. With teflon plates, well defined glasses could not be formed. Strong room-temperature fluorescence (RTF) and room-temperature phosphorescence (RTP) were obtained from benzo(f)quinoline(B(f)Q) and 4-phenylphenol(4-PP). Although RTF and RTP signals from B(f)Q in glucose glasses or 90% glucose/NaCl glasses were weaker compared to those signals obtained with 90% trehalose/NaCl glasses, the signals were strong enough for solid-matrix luminescence analysis. Several aspects of the sample preparation technique and sample holders will be discussed.

243 **DETERMINATION OF TOXIC METAL IONS USING OPTICAL FIBER METAL PROBES AND NEAR-INFRARED COMPOUNDS.** **A.Casay Guillermo, Dai Dong and Gabor Patonay, Georgia State University, Department of Chemistry, University Plaza, Atlanta Georgia, 30303.**

The determination of toxic metal ions using an optical fiber metal detector (OFMD) with near-infrared dyes will be reported. Several cyanine and naphthalocyanine derivatives with absorption and fluorescence maxima above 700 ran have been evaluated for the detection of lead, cadmium and other toxic metals. The NIR dyes were first entrapped in a permeable polymer matrix which allow the diffusion of small metal ions inside the matrix while at the same time prevented the dye from leaching. The matrix was placed at the distal end of two optical fibers that served as the reaction phase. The ability of the dye to complex with the metal ions is dependent on the diffusion of the metal ions in the matrix. As metal ions diffused through the matrix, the ions formed a complex with the entrapped dye producing fluorescent intensity changes which is utilized as a calibration curve for the determination of metal ions in unknown samples. Commercially available laser diodes with output wavelengths around 750-780 nm were used to induce fluorescence in the complex and the signal was detected with silicon photodiodes. Detection limits using a conventional PMT detector and a silicon photodiode detector will be presented. The stability of the optical fiber probe and the matrix was investigated by following the fluorescence response for several weeks. The association constant of the dye/metal complex will be discussed. Advantages of using the NIR region for the detection of these metal ions will be evaluated. The use of optical fibers with fluorescence probes in the near-IR region can expand the utility of enviromental measurements for water and ground water determination of toxic metals.

244 RELATIONSHPS BETWEEN THE HEAT CAPACITIES OF SOLID MATRICES AND THE LUMINESCENCE PARAMETERS OF ADSORBED PHOSPHORS. **S. M. Ramasamy and R. J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.**

Luminescence parameters of phosphors adsorbed on solid matrices were correlated with the heat capacities of the solid matrices over a wide temperature range. The systems investigated included p-aminobenzoic acid adsorbed on pure sodium acetate, 50%, 5% and 1.4% sodium acetate/sodium chloride mixtures, and benzo(f)quinoline and 4-phenylphenol adsorbed on 30% p^cyclodextrin/sodium chloride mixture. Phosphorescence lifetimes, and the fluorescence and phosphorescence intensities of the three phosphors on the five solid matrices were obtained in this work. Using quantum yields and lifetimes of the singlet and triplet states of the lumiphors, radiative and non-radiative rate constants were calculated. Excellent correlations were developed with the luminescence data and the heat capacity data. One of the most important relationships developed was between the phosphorescence lifetimes and the non-radiative rate constants from the triplet states of the phosphors. These data were, in turn, related to the heat capacities of the solid matrices. Several aspects of the relationships developed between the phosphorescence lifetimes, non-radiative rate constants and heat capacities will be discussed.

245 THERMAL AND OPTICAL PROPERTIES OF AMORPHOUS METAL COMPLEXES OF MONO AND DICARBOXYLIC ACIDS. **Richard S. Turk and Joel I. Dulebohn, Michigan Biotechnology Institute, 3900 Collins Rd., Lansing, Michigan *48909.***

Several materials such as low temperature glasses, oxide and polymeric glasses, and surface substrates are usually employed as hosts to enhance phosphorescence of molecules in the triplet state and limit nonradiative processes. Alkaline earth metal complexes of mono and dicarboxylic acids have been fabricated in our laboratory as optically transparent amorphous materials that promote intense room temperature phosphorescence. The use of Group II metals increases the rate and efficiency of intersystem crossing to the triplet state. In many cases, for a given metal, the luminescence intensity changes several orders of magnitude after substitution with a carboxylic acid of higher or lower molecular weight These metals also undergo ligand substitution reactions with competing coordinating ligands such as water that influences both the electronic coupling and the thermal properties of the solid. Material properties of the glassy state derived from X-ray diffraction and differential scanning calorimetry are compared to the phosphorescence intensities and lifetimes of selected metal and ligand pairs. The applications of these materials in food and pharmaceutical identification and analysis are discussed.

246 **X-RAY INDUCED LUMINESCENCE IN VITREOUS** SiO_2t, Allen J. Miller and Robert G. Leisure, Colorado State University, Fort Collins, CO 80523, USA

Vitreous SiO_2 undergoing x-irradiation emits visible light during irradiation. We have studied this effect in various samples of v-SiO_2 with different OH concentrations and thermal histories. In particular, dose dependence of the luminescence over the range from 0 to 750 Mrad (SiO_2) front surface dose by irradiation from a copper anode x-ray tube was studied. The luminescence spectra contain several bands, the intensities of which show a strong dependence on OH concentration, thermal history, and dose. For example, the 1.9 eV band intensity shows very different behavior between Suprasil-1 and Suprasil-W. Comparisons will be made between these luminescence features and electron spin resonance signals.

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247 **A SPECTROSCOPIC STUDY OF PHOTODEGRADATION OF ETHYLENE-VINYL ACETATE (EVA) COPOLYMER ENCAPSULANT FOR PV MODULES.** **F. J. Pern. National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401**

Fluorescence, UV-visible transmission, and spectrocolorimetric measurements were performed to characterize the structural changes and progress of discoloration of the ethylene-vinyl acetate (EVA) module encapsulant upon accelerated exposure. The EVA films were laminated and cured between two glass slides and exposed to a concentrated Xe light or an enhanced UV light source. The results from UV-vis measurements indicate that the discoloration is accompanied by a loss of the UV absorber, Cyasorb UV 531. The rates of Cyasorb loss and discoloration are greater for the EVA films (Formulation A9918) that are cured (cross-linked) longer with a greater concentration of UV-excitable chromophores produced than those EVA films (Formulation 15295) cured for less time with considerably fewer chromophores produced. The photodegradation results in a color appearance from a light yellow initially to a brown color later due to the formation of polyenes in the EVA films. Results of color indices measurements show that transition from light yellow to light brown is a fairly quick process and that from the light brown to a darker brown color is a slow and linear process. The latter requires a transformation of the initial shorter chromophores to longer ones as the exposure time lengthened, as determined from fluorescence and UV-vis analyses.

8 **LUMINESCENCE STUDIES OF THE METAL-CARBON MULTIPLE BOND IN PhC=Os(NH$_3$)^+.** **Scott Trammell. L. Mark Hodges, W. Dean Harman, and B. Pat Sullivan, University of Wyoming Department of Chemistry, Laramie, Wyoming 82070**

Transition metal complexes which contain metal ligand multiple bonds have an extensive ground-state chemistry that has grown in recent years. The excited state chemistry of these compounds is less developed. Of importance in understanding the excited state chemistry of metal complexes with metal ligand multiple bonds is the characterization of the electronic structure of the excited state. Luminescence spectroscopy is a powerful tool for investigating these types of excited states. Here, we will present our recent luminescence studies of the Osmium (VI) carbyne complex, PhC=Os(NH$_3$)$_5^{3+}$

LUMINESCENCE AS A PROBE FOR STUDYING PHOTOINDUCED ELECTRON TRANSFER WITH PEPTIDES AS INTERVENING MEDIA L. E. Peitersen, B. P. Sullivan, Department of Chemistry, University of Wyoming, Laramie, Wyoming, 82070.

Electron transfer within biological systems is an area of debate in the current literature. The controversy centers about whether the mechanism of electron transfer occurs by way of a special pathway within the protein or by nonspecific routes. We will present conclusions from our recent studies involving electron transfer from the excited state of Ru(bpy)3^{2+}*, where bpy is 2,2'-bipyridinium, to a series of viologen electron acceptors (luminescence quenchers) in an environment of short polymers covalently bound to an organosiloxane film. Results will be interpreted in light of previous work by our group in which long-distance electron transfer from Ru(bpy)3^{2+}* to these quenchers in non-biological systems.

250 MICRO-LC/ELECTROSPRAY MS AT NANOLITER FLOW RATES: ULTRA-HIGH SENSITIVITY FOR TRACE ANALYSIS. Richard M. Caprioli. Department of Biochemistry and Molecular Biology and Analytical Chemistry Center, University of Texas Medical School, P.O. Box 20708, Houston, TX 77030.

Many compounds endogenous in biological systems are present at trace levels and are in dynamic flux. This presents impressive challenges to the analyst in terms of monitoring these changing concentrations and also their quantitation. We have developed a micro-electrospray source which integrates nanoliter-flow capillary LC to provide direct analysis of aqueous samples at concentrations below 1 fmol/uL. In the case of neurotensin, a neuropeptide, detection can be accomplished at < 10 attomole/uL in samples in physiological salt solution. For proteins in the 20,000 - 60,000 Da range, sensitivities in the 5-10 fmol range for total amount injected were obtained. One of the dynamic biological systems discussed will be microdialysis/MS for ***in vivo*** monitoring of natural metabolites. With the high sensitivity ***i~ES*** MS, endogenous release of neuropeptides in freely-moving animals has been achieved. The overall technique will be discussed in terms of its potential use in neurochemical and pharmacological studies.

251 **MATRIX ASSISTED LASER DESORPTION: HOW "SOFT" AN IONIZATION PROCESS?** **Robert S. Brown and John J. Lennon, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300**

Matrix assisted laser desorption (MALD) has been known since it's initial introduction as a "soft" ionization process producing almost exclusively intact pseudomolecular analyte ion species. Actually, a significant amount of delayed analyte fragmentation occurs in the MALD process, but is typically not observed with continuous extraction (linear) time-of-flight (TOF) mass spectrometers. Post source decay fragmentation can be observed in reflector based TOF mass spectrometers by careful tuning of the reflector energy, but can focus only a small mass range of fragments for any given reflector energy. This fragmentation occurs in the field free flight tube of the instrument after the source and prior to the reflector (mircosecond time scale). By utilizing delayed, pulsed ion extraction and a linear TOF instrument, relatively prompt (<350 ns) sequence specific fragmentation can be observed with MALD generated peptide/protein ions. For example, the B chain of bovine insulin produces amide bond (and side chain) cleavages (both C and N terminus). Only C terminal amide bond cleavage, however, is observed for the larger cytochrome C. The abundant fragment ions produced can be studied by this approach under a single set of conditions, producing mass accuracies of better than +0.3 Da. The matrix used has a pronounced effect on the degree of fragmentation. This suggests a chemical and not a collisional process(i.e., unimolecular decay) is involved.

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DETECTION OF VOLATILE ORGANIC COMPOUNDS IN AIR AND WATER SAMPLES BY APCI TOFMS. **Alex F. Schreiner. Chung Hang Sin, and Jon W. Carnahan, Northern Illinois University, Department of Chemistry, DeKalb Illinois, 60115.**

The analysis of volatile organic compounds in gaseous and aqueous samples is achieved using an atmospheric pressure chemical ionization (APCI) source coupled with an orthogonal time of flight mass spectrometer (TOFMS). The samples are introduced into the APCI via a GC for the gaseous samples and by a head space purging device for the aqueous samples. The compounds are ionized by a glow discharge (helium plasma), which can be controlled by the flow and temperature conditions in the APCI. Parent and protonated parent ions are observed for most compounds, but considerable fragmentation does occur in some cases. The quantitation of molecules is dependent on the atmospheric chemistry and the ion transmission into the vacuum.

Although glow discharge is an efficient ionization source for quadrupole and sector instruments, there are disadvantages when it is coupled to a TOFMS. In this case the use of an orthogonal reflectron TOFMS has Jed to an increased duty cycle over the original model introduced by McClaren. The optimization for benzene analogs resulted in mid ppb detection limits for the gaseous samples. The aqueous samples showed a dependence on the volatility of each particular compound, since they were introduced by head space purging.

EVALUATION OF A MOBILE QUADRUPOLE ION TRAP MASS SPECTROMETER (CBMS) DESIGNED FOR DETECTION OF MICROORGANISMS IN THE ENVIRONMENT. **Curtis D Mowry. Franco Basile, and Kent J. Voorhees, Colorado School of Mines, Dept. of Chemistry and Geochemistry, Golden, Colorado, 80401.**

The Chemical/Biological Mass Spectrometer (CBMS) detector consists of an impactor/pyrolyzer, transfer line, membrane separator, and a quadrupole ion trap mass spectrometer. Ambient air is used as the buffer gas. Characteristic products (biomarkers) of pyrolyzed airborne microorganisms can be observed in the mass spectra collected by the CBMS. The CBMS, however, has varying detection limits for different biomarkers, which range from amino acids to carbohydrates and fatty acids. For effective determination of microorganisms, the factors affecting biomarker detection limits must be determined and characterized. Instrumental modifications including a gas chromatographic interface, new vacuum system, and non-membrane sample introduction, have been implemented to evaluate the effects on detection limits by system components. This component evaluation as well as detection limits for test compounds and biomarkers will be discussed in terms of future modifications to the CBMS, and its capabilities as a mobile environmental mass spectrometer.

254 **GAS PHASE CHEMISTRY OF SIMPLE BORON IONS**

Joseph A. Hankin, Ed Motell, C. H. DePuy, and Robert Damrauer, Department of Chemistry, University of Colorado at Boulder, Boulder, Colorado 80309-0215.

A Flowing Afterglow - Selected Ion Flow Tube (FA-SIFT) instrument uses a quadrupole mass filter to select out specific ions formed in a flowing afterglow plasma. (VanDoren, J.M.- Barlow, S.E.; DePuy, C.H.; Bierbaum, V.M. *J. Am. Chem. Soc.* 1987, 109, 4412) These ions are entrained in a thermalizing flow of helium and injected into a reaction flow tube where they can be characterized by their dissociation products and by their chemistry with a variety of neutral reagents. The gas phase chemistry of several unusual boron ions has been studied with the FA-SIFT, including $[B_2H_3]^-$ and $[B_3H_6]^-$. (Krempp, M. R.; Damrauer, R.; Keheyan, E.; DePuy, C.H. *J. Am. Chem. Soc.* in press.) Recent work has involved studies of several simple boron cations $[B]^+$, $[BH]^+$, and $[BH2]^+$. A description of this versatile instrument with its creative use of mass spectrometry components along with a discussion the chemistry of simple boron cations will be presented.

255 **POLYCYCLIC AROMATIC HYDROCARBONS: FROM THE LABORATORY TO INTERSTELLAR SPACE.** **Christopher M. Hadad. Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215.**

Some prominent and intense absorption features in the interstellar medium are called the diffuse interstellar bands (DIBs). They have long perplexed astronomers with regard to what molecular species are responsible for these ubiquitous features. Polycyclic aromatic hydrocarbon (PAH) cations are considered by some to be the carriers of the DIBs. The structural variety of the PAHs, from naphthalene to pyrene and beyond, allows different carriers of the DIBs, and the low ionization potential of these aromatic compounds assures that these species will be ionized in the interstellar medium where the DIBs are found. The absorption spectra of some of these species under matrix isolation conditions support the idea of PAH cations as the carriers of the DIBs. In order to confirm these results for the gas phase, we have initiated laboratory studies to prepare some PAH cations in sufficient density in order to obtain their absorption spectra. Preliminary experiments towards this goal will be presented.

256 **MEASUREMENT OF LONG-CHAIN FATTY ACYL COENZYME A BY GC/MS.** **Keith L. Clay. Christopher A. Johnson, and Robert C. Murphy, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson St., Denver, Colorado 80206**

Coenzyme A thioesters are not sufficiently volatile for direct GC/MS analysis and require, therefore, degradation and derivatization for analysis. A procedure devised for the GC/MS analysis of the long-chain fatty acyl-CoA (LCFA-CoA) thioesters utilized reductive cleavage of the thioester bond to give the corresponding alcohol with derivatization of the alcohol for GC/MS. Another procedure used glycine aminolysis to cleave the fatty acyl group as the amide with subsequent derivatization of the free carboxyl for negative ion chemical ionization GC/MS. We have evaluated these procedures for application to biological extracts and found them to suffer from unacceptable contamination and cross-reactions with biological compounds. A new procedure which simultaneously cleaves and derivatives the fatty acyl groups has been developed which utilizes the unique chemistry of the thioester bond to give the requisite specificity for GC/MS analysis. Heptafluorobutylamine directly forms the amide of the fatty acyl groups in thioester linkage to CoA, catalyzed by silver ion. The reaction is specific for thioesters and gives a derivative which is well-suited to GC/MS analysis.

257 **DIFFERENTIATION OF MICROORGANISMS BY PYROLYSIS-MASS SPECTROMETRY AND PATTERN RECOGNITION OF FATTY ACID METHYL ESTER EXTRACTS.** **Franco Basile[1]. Te« L. Hadfiled[2], and Kent J. Voorhees[1]. department of Chemistry, Colorado School of Mines Golden CO 80401; [2]Armed Forces Institute of Pathology, Washington, D.C. 20306-6000**

In this study Curie-point pyrolysis-mass spectrometry (Py-MS) with pattern recognitior (Principal Component Analysis, PCA) has been used to differentiate microorganisms based or their fatty acid distribution. PCA of normalized and autoscaled mass spectra differentiate! microorganisms studied according to Gram type, at the genus level, and at the species leve Loading plots of the PCA showed that Gram negative bacteria was characterized by a large palmityl signal than the pentadecanyl and lauryl-methyl esters. For Gram positive bacteria, tht-signal of the branched FAME 12-methyltetradecanoyl (aC15:0, m/z 256, a= anteiso) was highe than the palmityl signal. Separation of the microorganisms at the genus and species level wat based mainly on the relative abundance of unsaturated fatty acids to 3-hydroxy fatty acids Results will be shown for the trimethvlphenylammonium in situ derivatized whole microorganism: and compared with both FAME-extract, Py-MS and GC/FAME analyses.

258 **ANALYSIS OF BEESWAX BY PYROLYSIS MASS SPECTROMETRY.** **Michael B. Beverly. Paul T. Kay, and Kent J. Voorhees, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401**

The influx of Africanized bees from South America has generated an interest and need for a technique to rapidly identify the species of bee infesting a hive. Beeswax is a complex mixture of saturated and unsaturated hydrocarbons, esters, and acids, whose composition has been shown to vary with the species of bee. Pyrolysis mass spectrometry (Py-MS) has been conducted on beeswax from several species of bees to determine the feasibility of using this technique as a rapid method for bee identification. Waxes examined include those from the Asian species Apis dorsata, Apis florea, and Apis cerana, the European species Apis mellifera, and the Africanized European, Apis mellifera scutellata. Each wax produces a characteristic Py-MS fingerprint that can be used for identification. Multivariate statistical analysis of the Py-MS data revealed which chemical components were responsible for species differentiation. The Py-MS fingerprints of each species, the multivariate statistical analysis, and chemical components enabling differentiation will be presented. Preliminary results regarding the application of Py-MS in identifying archeological wax obtained from a native American excavation will also be presented.

259 **IDENTIFICATION OF LIPID METABOLITES FROM HUMAN EOSINOPHILS BY MASS SPECTROMETRY.** **Denise K. MacMillan and Robert C. Murphy, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson St., Denver, Colorado 80206**

Human eosinophils are white cells in the blood that have the capacity to generate metabolites of arachidonic acid by the action of two different oxygenases, 5-lipoxygenase, the first enzyme involved in the formation of leukotrienes, and 15-lipoxygenase, which forms 15-HPETE. The first enzymatic product of 5-lipoxygenase is 5-HPETE and we have investigated the metabolism of this reactive metabolite of arachidonic acid when it is a substrate for the 15-lipoxygenase. Identification of the metabolites has been carried out using mass spectrometry and the identification of various conjugated trienes has been of particular interest. Identification of the position of oxygen substitution of the arachidonic acid backbone has been determined following catalytic reduction of these compounds followed by derivatization and GC/MS under electron capture negative ion chemical ionization conditions. Major products of the action of recombinant 15-lipoxygenase acting on 5-HPETE have been characterized as 5,15-dihydroperoxyeicosatetraenoic acid as well as 5,12-dihydroxyeicosatetraenoic acids indicating the intermediacy of LTA_4.

260 **COLLISION INDUCED DISSOCIATION OF OXIDIZED PHOSPHOLIPIDS.** **Kathleen A. Harrison and Robert C. Murphy, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson St., Denver, Colorado 80206**

Oxidized phospholipids formed *in vivo* during free radical induced lipid peroxidation may be important lipid mediators. Oxidized phospholipids from *in vitro* sources can activate cells through the platelet activating factor receptor. Prostaglandin-like molecules can also be formed *in vivo* by free radical oxidation of phospholipid esterified arachidonic acid. Phospholipase hydrolysis of these iso-prostaglandins may also represent a non-enzymatic source of lipid mediators. To better understand the roles of oxidized phospholipids, the active molecules must be identified and measured. Fast atom bombardment ionization with tandem mass spectrometry is a sensitive and specific technique for the analysis of complex mixtures of phospholipid molecular species. Fundamental and unusual aspects of the collision induced dissociation of oxidized phospholipids will be presented in the context of identifying various classes of oxidized phospholipids, including acyl chain-shortened molecular species and multi-oxygenated species. The model system used to produce oxidized phospholipids is hemoglobin induced oxidation of palmitoyl-arachidonoyl glycerophosphocholine.

261 **PYROLYSIS MASS SPECTROMETRY OF GLYCYL DIPEPTIDES: STERIC AND ELECTRONIC EFFECTS ON THERMAL CYCLIZATIONS.** **AlanD. Hendricker. B. Murugaverl, and Kent J. Voorhees, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401**

A comprehensive study has been performed on 39 dipeptides containing glycine (as either the C- or N-terminal amino acid) using pyrolysis tandem mass spectrometry. The results indicate that thermal cyclization products formed during pyrolysis are affected by the structures of the amino acid bonded with glycine in the dipeptides. Several factors, including steric and electronic effects and the charge state of the N-terminus can alter the extent to which the cyclization process occurs. A correlation is observed between the size of the side chain attached to the amino acid paired with glycine and the relative yield of cyclic diketopiperazines formed during pyrolysis. In addition, electronic effects created by heteroatoms in certain side chains can hinder or aid in the cyclization process, based on their location and nature. The fragmentation mechanisms of glycyl dipeptides will be presented and the factors which can affect thermal cyclizations will be discussed.

262 **GAS-PHASE CHEMISTRY OF SILACARBONYL ANIONS**

Robert Damrauer and Joseph Hankin, Department of Chemistry, University of Colorado at Denver and Boulder, Denver, Colorado 80217.

Flowing Afterglow -Selected Ion Flow Tube (FA-SIFT) technology has been used to study several new silicon analogs of carbonyl compounds. These gas-phase studies, as well as closely related computational studies, will be presented.

263 THE SN2 MECHANISM: FROM GAS PHASE TO SOLUTION.

Gustavo E. Davico. Charles H. DePuy and Veronica M. Bierbaum., Department of Chemistry and Biochem., University of Colorado at Boulder, Campus Box 215, Boulder, Colorado 80309-0215.

The SN2 mechanism is probably the most widely studied reaction mechanism. Nevertheless, there are no experimental data of the kinetic isotope effects for the micro-solvated processes. The Selected Ion Flow Tube (SIFT) technique was used to obtain rate coefficients for the reactions of F^- and F"(solvent) (where solvents H_2O, D_2O, CH_3OH, CH_3OD, CD_3OH, CD_3OD, HF, DF, $(CH_3)_2CHOH$ and $(CH_3)_2CHOD$) with CH_3X (where X= Cl, Br and I). *Inverse* kinetic isotope effects were found for deuteration of the solvent molecule with kH/kD as small as 0.59 (k[F'(CH30H) + CH3Br]/k[F"(CD30D) + CH3Br]).
In keeping with previous results, inverse kinetic isotope effects were also observed for deuteration of the methyl halides. Kinetic isotope effects were also measured for the reactions of several different nucleophiles with alkyl halides. The results will be discussed in function of the nucleophile nature (basicity, oxygen or sulphur centered anion, etc.) as well as possible substitution/elimination mechanisms.

264 **$CACL^+$ AND HIGH PRECISION $^{87}Sr/^{86}Sr$ MEASUREMENTS**

E.Craig Simmons, Dept. Chemistry & Geochemistry, Colorado School of Mines, Golden, CO 80401; Kathleen R. Simmons, U.S. Geological Survey, Federal Center, Denver, CO 80225

Modern geochemical studies using $^{87}Sr/^{86}Sr$ ratios require the ability to resolve differences on the order of 3 parts per 100,000 *(2a).* TIMS measurements using $SrCl_2$ in a multiple filament source yield stable and easily adjusted signals. The major isobaric interference is ^{87}Rb (corrected using ^{85}Rb). It has been found that $CaCl^+$ can occur at the same temperatures as Sr^+; masses range from 75 (73.2%) to 85 (0.044%); 75/85=1663. While producing no direct isobaric interference on the Sr^+ mass spectrum, the presence of $CaCl^+$ produces 'extraneous' 85, which is then included in the correction of ^{87}Sr. Masses of $CaCl^+$ in the vicinity of the Sr spectrum (81, 83 & 85) are all minor (< 1%), and no mass 84 occurs. Thus, the presence of $CaCl^+$ may not be detected on visual scans of the mass spectrum, or by measurement of $^{84}Sr/^{86}Sr$ ratios. A 10 ppm addition to a ^{87}Sr signal of $5x10^{-12}$ amp involves an 'extraneous' 85 signal from $CaCl^+$ of only $1.3x10^{-16}$ amp (820 ions/sec), which would be manifested in 83 = $5.4x10^{-16}$ amp (undetectable) and 75 = 2.2x10"" amp (easily detectable). Sr-isotope measurements of this kind should also include a check in the vicinity of mass 75.

265 STABLE ISOTOPE TRACERS - ADVANTAGES OVER RADIOTRACERS

E.Craig Simmons, Dept. Chemistry & Geochemistry, Colorado School of Mines, Golden, CO 80401

An integral part of studies in chemistry and environmental science, radiotracer studies require the availability of a radioactive isotope of the appropriate element, with a suitable half-life. These requirements can place severe restrictions on: the subject to which the experiment is applied (safety considerations), which elements can be studied (many elements have no suitable radioactive isotopes), and the time scale of the experiments (must have detectable amounts of radioactivity).

These limitations can be overcome with stable isotope ratios, using a sample of the element enriched in a minor isotope, which is used in the place of a radiotracer. The abundance of the tracer is obtained mass spectrometrically, using the appropriate modifications of the standard isotope dilution equation. This approach can: (1) Eliminate safety & licensing requirements associated with radioactive isotopes; (2) Eliminate the half-life limitations on experiments; (3) Apply to elements for which no suitable radioactive isotopes are available; (4) Take advantage of the fact that the overall abundance of the tracer is constant and does not decay with time.

CHARACTERIZATION OF ABSORBED WATER IN PERDEUTERATED POLYCARBONATE BY RESIDUAL-PROTON NMR. **Patricia Lani Lee and Jacob Schaefer, Department of Chemistry, Washington University, St. Louis, MO 63130.**

The residual protons in perdeuterated polycarbonate give rise to a high-resolution solid-state NMR spectrum. Signals from the remaining 1% polymer protons and fully protonated absorbed water are well resolved. The chemical shift of the water is indicative of isolated H 2 O molecules surrounded by an organic matrix. Spinning sideband intensities show that the water undergoes rapid, nearly isotropic rotational reorientation. As determined by *H observe, ^{13}C dephase rotational-echo double resonance NMR, translational motion of the water is restricted in a powder sample but not in an annealed thin film. In a powder sample, the average distance between water protons and the nearest ^{13}C-labeled carbonyl carbon was found to be 5 ± 1 A.

266 XENON NMR IN POLYMERS. J. B. Miller. C. M. Roland, J. H. Walton", and J. M. Snowed, Code 6122, Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5342

Although xenon is essentially chemically inert, its chemical (physical) shift is very sensitive to its physical surroundings. Recently in other laboratories, ^{129}Xe has been used as an NMR probe nucleus for the study of zeolites and surfaces. We have investigated xenon as a probe to characterize polymers and polymer blends. The sensitivity of the ^{129}Xe chemical shift to the environment about the atom leads to variations in the chemical shift with polymer chemistry, as well as a strong temperature dependence. We have used the ^{129}Xe chemical shift and its temperature dependence to determine the miscibility of polymer blends and to study phase transitions in polymers. Theories of the chemical shift of a solute (Xe) in solvents (polymers) allow us to investigate the interactions of the constituent polymers in miscible blends.

[1]NRC/NRL postdoctoral associate.

^Present address: Department of Chemistry, Florida State University, Tallahassee, FL 32306

267 CHARACTERIZING SURFACE POLYMERS WITH NMR. **J. P. Burgess, Research Triangle Institute, Research Triangle Park, NC 27709 and E. O. Stejskal, Department of Chemistry, Box 8204, North Carolina State University, Raleigh, NC 27695-8204**

The combination of cross polarization (CP), high power resonant proton decoupling, and magic angle sample spinning (MAS) makes it possible to obtain liquid-like, high resolution rare spin NMR spectra in many diverse kinds of organic solids. The interactions between polymers and the surfaces of inorganic solids are important in the chemistry and physics of materials. High resolution solid state NMR methods, especially CPMAS, can be applied to such systems so long as the specific surface area is large enough to provide enough polymer to study and the surface layer thin enough that most of the observable specimen lies near the surface. We chose to study methacryloxy propyl silanized silica and styrene. These two species were polymerized (to different extents) separately, sequentially, or simultaneously, to produce surface layers with different structures. In all cases, an intrinsically inhomogeneous organic phase resulted. First we used ^{29}Si and ^{13}C CPMAS NMR to study the primary chemistry of the surface reactions. Then we used CPMAS with interrupted decoupling and measured both $T_{ip}(^{13}C)$ and $T_{ip}(^{1}H)$ to examine the inhomogeneity of the surface polymer with respect to both motion and structure. We found at one extreme surface block copolymers and at the other extreme nonbonded polyblends. We detected different degrees of layering. The methodology used to arrive at these models will be discussed.

268 SPATIALLY RESOLVED DETERMINATION OF MATERIALS PROPERTIES BY NMR-IMAGING

W. Kuhn*, S. Hafher*, P. Barth*, P. Denner+, S. Simon*, *Fraunhofer Institute for Biomedical Engineering, Magnetic Resonance Division, Ensheimer Str. 48, D-66386 St. Ingbert, +Hochschule Erfurt, Nordhauser Str. 29, Erfurt, *Varian GmbH, Alsfelder Str., Darmstadt, Germany

Spatially resolved NMR investigations of elastomers have been applied to characterize changes in the network structure of technical elastomers. To express NMR parameters in terms of materials properties one requires a suitable theory connecting NMR relaxation times to materials parameters such as e. g. crosslink density, defect size, defect diffusion coefficients etc. For elastomers such theories are already existent and in many cases proven to be useful. The aim of this work is to demonstrate the potential of NMR imaging for spatially resolved determination of material properties. T_1, T_2 and $T_{1\rho}$-imaging experiments were performed on aged technical rubber samples and of such with different crosslink densities as well. The NMR data were analyzed using the BPP and Anderson-Weiss theory (BPP-AW) and the theory of Limited Translational Defect Diffusion (LTDD). The results reveal the different frequency components of the molecular motion, the non averaged dipolar interaction $q*M_2$ and the crosslink density. From LTDD-theory the defect size of chain entanglements, diffusion distance and defect diffusion coefficients could be derived. Furthermore, histogram analysis of all parameters derived from the data evaluation shows clearly crosslink density inhomogeneities.

NMR STUDIES OF STRUCTURE AND DYNAMICS IN MACROMOLECULAR SOLIDS. Bradley F. Chmelka, AN Firouzi, Manfred Wilhelm, Heather Maynard, and Sean Williams; Department of Chemical and Nuclear Engineering, University of California, Santa Barbara, CA 93106

Recent experimental results will be presented from NMR studies of orientational order, relaxation, and heteronuclear couplings in macromolecular materials. Systems under investigation include liquid crystals, oriented fibers and thin films, conducting polymers, and surfactant-inorganic composites, materials that are characterized by order/disorder at length scales varying from the molecular to the macroscopic. The governing influences of local structure and dynamics on the macroscopic properties of these complicated materials are being investigated using new and conventional magnetic resonance techniques, including multidimensional DECODER and relaxation measurements. New developments in these areas will be discussed, highlighting applications to novel macromolecular systems.

270 STRATEGIES FOR THE ANALYSIS OF NON-CRYSTALLINE SYNTHETIC AND BIO-POLYMERS BY SOLID STATE NMR AND ATOMIC FORCE MICROSCOPY. **Tomasz Kowalewski and Jacob Schaefer, Department of Chemistry, Washington University, St. Louis, MO 63130.**

The absence of long-range order in noncrystalline nanostructured materials dictates the need to characterize their structure over distances ranging from angstroms to tens of nanometers. We describe a recently developed strategy in which this range is covered by joint use of solid state NMR and atomic force microscopy (AFM). Application of this strategy to synthetic polymers will be illustrated with the results of studies of interfaces in immiscible blends. Distances across buried interfaces measured by REDOR NMR are interpreted with the aid of AFM observations of nanoscale roughness of polymer surfaces. In studies of biopolymers, REDOR NMR is used to map the binding sites of enzymes immobilized as glassy solids by dehydration. A primary concern in this effort is that dehydration may have resulted in destruction or perturbation of the native structure. AFM studies show that the preservation of native structure correlates with the nanoscale morphology of the protein glass. Future work on biopolymers will involve using AFM to image single protein molecules under native and dehydrated conditions. Information about the global shapes of protein molecules and their changes due to substrate binding or change in external conditions will be used to complete the local picture provided by REDOR NMR.

271 ROTATING FRAME NMR MICROSCOPY. **Klaus Woelk. Jerome W. Rathke, and Robert J. Klingler, Argonne National Laboratory, Chemical Technology Division, 9700 South Cass Avenue, Argonne, Illinois 60439.**

A new NMR microscopic method, Rotating Frame Microscopy *(RFM),* has been developed to provide high-resolution chemical-shift information while simultaneously resolving distances down to a few micrometers. The method uses the confined, strong, and mathematically well-defined B_r gradient that can be found in especially designed toroid cavity detectors. As shown from results in 'H-, ^ " C - , and ^{19}F-NMR spectroscopy, RFM is useful in determining the relationship between chemical structure and depth for coatings deposited inside the detector. High-pressure and high-temperature capabilities of toroid cavity probes enable measurements of penetration rates in polymer or ceramic films *in situ* under various conditions. Additionally, electrochemical processes can be monitored, when the central conductor is used as a working electrode. A major advantage of the RFM method is that the resonance frequencies of the spins are not manipulated to be the measure of distance. Thus, chemical shift and distance can easily be resolved simultaneously. Furthermore, the distance resolution is, to a first approximation, independent from the NMR-frequency linewidth. Therefore, RFM is especially attractive for investigations of solids and polymers, where broad lines usually limit the spatial resolution to 50-100 *fim.* An additional advantage of toroid cavity detectors is their high NMR sensitivity, so that even small voxels can be investigated without accumulating large numbers of spectra.

272 DECRYPTING THE CHEMICAL SHIFT CODE IN PROTEINS: A QUANTUM CHEMICAL APPROACH TO STRUCTURE IN SOLIDS AND LIQUIDS. **Eric Oldfield. Angel C. de Dios, Hongbiao Le, John G. Pearson and Chenyang Lian, Department of Chemistry, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, IL 61801.**

The chemical shift is the most readily observed spectroscopic parameter in most systems, but probably one of the more difficult to interpret. We will show, however, that it is now possible to accurately predict isotropic chemical shifts of most heavy nuclei in proteins. For ^{13}C and ^{15}N, <J>,Y,% torsional effects dominate shielding, and shielding or chemical shift surfaces, 8(<{),\j/,x), permit a rapid way of predicting experimental shifts from known structure. In the case of the presence of internal motion, shielding trajectories can be constructed. A new approach to deriving structural information about proteins will also be presented. The method is based on measurement of a spectroscopic parameter, P, (such as a chemical shift or a spin-spin coupling), which is then transformed via use of a parameter surface, P(a,|3), into a prediction or Z-surface, Z(a,(3). Using six empirically determined surfaces, the backbone (J),\|/ error is about 15°, but for 36 Ala residues in *Staphylococcal* nuclease, ribonuclease H, calmodulin and interleukin-ip, this reduces to -12° when only quantum mechanically computed ^{13}C shielding and experimental $^{i}H^{\alpha}$ shift surfaces are utilized. The Z-surface approach permits unique combination of a wide variety of spectroscopic observables for structure refinement and prediction. Experimental applications to several systems will be presented.

RECENT PROGRESS IN ^{113}CD NMR OF BIOLOGICAL SYSTEMS...MODEL COMPOUNDS, HEMOGLOBIN, AND FUN & GAMES WITH BONES. **Paul D. Ellis. Andrew S. Lipton, Kate McAteer, Breege A. Concannon, Scott Mason, Roy Wuthier, Dan Reger, Rodolfo Santos, and Robert A. Wind. Pacific Northwest Laboratory, P. O. Box 999 Richland, WA 99352. and Dept. of Chem. and Biochem., University of South Carolina, Columbia, SC 29208.**

The technique of substituting "$^{3}Cd^{+2}$ into a metalloprotein as a spin-spy has been widely used: however, interpretation of the resulting spectra can be difficult without extensive knowledge of the effects of certain coordination environments. Hence, there is a need for compounds that can be used as models of the metal center of the protein. In this presentation, we describe a new class of compounds that can be used to model nitrogen coordination environments of metalloproteins. The family of poly(pyrazolyl)borate ligands generates stable complexes with cadmium that allow various coordination environments about the metal center. The number of donor nitrogen atoms can be varied by going from the dihydrobis-, hydrotristo tetrakis(pyrazolyl)borate ligands. The principal elements of the $^{1)3}$Cd shielding tensors have been determined for an N_4 and several N_6 coordination environments, thereby eliciting the effect of adding substituents to the pyrazolyl rings. A variety of mixed ligand donor atom combinations, such as N_3S_2, N_3H_2, and N_3C, have also been investigated. Other compounds of interest to be presented are the only reported cases of a cadmium hydride and a dimer that contains a cadmium-cadmium bond. If time permits, we will present current data on other systems of biological interest including the use of Cd^{2+} substituted porphyrins as a spin-spy in hemoglobin and the utilization of ^{U3}Cd NMR as a means to characterize Cd^{2+} substituted apatitic lattices.

274 **PHOTOCHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION IN SOLID STATE NMR SPECTRA OF REACTION CENTERS FROM PHOTOSYNTHETIC BACTERIA**

Martin Zysmilich and Ann McDermott, Columbia University, Department of Chemistry, NY NY 10027

Photochemically Induced Dynamic Nuclear Polarization has been observed in the solid state NMR spectra of photosynthetic reaction centers. Spectra of U- ^jsj (nonspecifically) labelled reaction centers exhibited emissive signals with intensities of approximately -300 times thermal polarization, but the polarization was observed only when the quinones (QA and Qg) were either prereduced or removed and when intense ilumination was applied (ca. 50 W of incandescent, white radiation). Spectra were collected with magic angle spinning; proton decoupling did not effect the observed line widths. We propose that the signals are from the tetrapyrrole nitrogens of bacteriochlorophyll dimer, P, that serves as an electron donor. The signals arise because non-equilibrium mixing of the singlet and triplet states of the initially formed charge transfer pair P+I- is partly driven by hyperfine interactions. Additional signals were observed from nitrogens in nearby parts of the protein (histidine and amide nitrogens).

^{27}**5 SOLID STATE NMR STUDIES OF NUCLEIC ACIDS,** **D. Gregory, J. Chang, D. Mitchell, S. Kiihne, J. Callahan, G. Drobny. Department of Chemistry, BG-10, Univ. of Washington, Seattle, WA 98195**

We will describe the application of solid state NMR techniques to the study of the structure as well as the dynamics of DNA oligomers containing A_nT_n and T_nA_n tracts. Such tracts undergo structural transitions to B' DNA (characterized by a very narrow minor groove), are implicated in DNA bending, and serve as transposition and replication origin sites. An advantage of solid state NMR is the ability to define the nature of localized motions over a wide dynamics range of rates. Coupled with optical and EPR data, a very complete picture of the internal motions of DNA may be obtained. In particular, solid state deuterium (^{2}H) NMR studies indicate pronounced mobility of certain deoxyribose rings within AT-rich tracts. The view of the dynamics of these sugar as derived by solid state 2H NMR will be compared and contrasted to the theories of sugar ring motion widely used to interpret the proton scalar coupling data derived by high resolution NMR multidimensional NMR methods.

The structural context of these dynamics can also be investigated by solid state NMR. Unlike high resolution NMR techniques, which derive interproton distances from NOE interactions that are dependent on the inverse sixth power of internuclear distances, solid state NMR techniques extract internuclear distances from static dipolar couplings, which are dependent on the inverse cube of internuclear distances. Numerous ^{13}C-^{13}C and ^{15}N-^{13}C distances between adjacent bases may be measured, at least in principle by solid state NMR methods, if appropriately labeled nucleosides can be produced. However, numerous interbase distances involve spin pairs which have large chemical shift anisotropics and virtually no difference in isotropic chemical shift. The performance of pulse sequences designed to suppress chemical shift anisotropics and a number of pulse imperfections will be discussed and their application to specifically labeled DNA oligomers will be described.

276 **PROTON NMR STUDY OF SEEDS.** **Cynthia F. Ridenour and Gary E. MacieL Department of Chemistry, Colorado State University, Fort Collins, CO 80523.**

High-resolution, solid-state ^1H NMR techniques were used to study various aspects of the chemical state of barley grains, including germination and aging. Proton MAS spectra reveal the water and lipid components and CRAMPS techniques provide spectra that reveal the protein and carbohydrate components, as well as water and lipid. Tj and T_2 measurements using MAS-only and CRAMPS techniques provide information about molecular mobility within the grains during imbibition. ^-'H spin-exchange techniques were used to probe hydration in germinating barley grains. Direct spectral evidence was obtained for the process of hydration of proteins and carbohydrates during imbibition. Evidence shows that water is motionally (as opposed to spatially) redistributed in grains following an imbibition period, probably to more tightly bound states. Qualitative conclusions on the consequences of imbibition were made, but quantitative evaluations are elusive.

277 **EXCHANGE PROCESSES IN ORGANIC CRYSTALS: CAN THE SOLID-STATE NMR AND DIFFRACTION RESULTS BE RECONCILED?** **Lucio Frydman, Department of Chemistry (M/Clll), University of Illinois at Chicago, Chicago, IL 60607.**

Diffraction measurements have led to the common opinion that apart from small atomic thermal vibrations, organic crystals resemble "molecular cemeteries" whose dynamic chemical processes are hardly worth analyzing. This view has been challenged during recent years by a series of solid-state NMR studies, which demonstrated that hydrogen-exchange or bond-rearrangement processes can escape from the rigidity imposed by the crystal packing forces. Noteworthy, many of the crystalline solids for which NMR revealed this kind of dynamics had been previously characterized via diffraction methods as composed by non-exchanging systems. Yet, as we discuss in this presentation, the diffraction and dynamic NMR results of these solids can still be reconciled if the observed structures are assumed to reflect weighted averages of the different tautomers involved in the chemical equilibria. The results from the two techniques can then be used in a complementary way to retrieve a description of the geometrical changes occurring along the reaction coordinate, with a degree of detail that is only matched by theoretical calculations. We illustrate the applications of these combined stractural/NMR analyses to our results on bridged annulenes and porphyrins, as well as to other dynamic NMR processes reported in the literature.

278 **DIPOLAR RECOUPLING IN SOLIDS UNDER MAGIC ANGLE SPINNING IN THE SPIN-LOCKING FRAME (DRAMSL).** **B.-O. Sun. P.R. Costa, D.Kocisko, P.T . Lansbury Jr., and R.G. Griffin, Francis Bitter National Magnet Laboratory and Chemistry Department, MIT, Cambridge MA 02139**

The dipolar coupling in rotating solids, averaged to zero by MAS, can be reintroduced in the spin-locking interaction frame by rotor-synchronized phase shifts of an applied spin-locking field by 90°. We call this new experiment DRAMSL (Dipolar Recovery At the Magic angle in the Spin-Locking frame), in analogy with the corresponding laboratory-frame experiment, DRAMA. Because the spin-locking fields both truncate and play the role of the chemical shift terms in the Hamiltonian, DRAMSL is insensitive to the chemical shifts as well as chemical shift anisotropics of the coupled spins. DRAMSL therefore can be applied to obtain two-dimensional correlation spectra, or alternatively it can be used as a double-quantum filter. Through numerical simulations of the magnetization exchange trajectory (e.g. the mixing time dependence of the cross-peak intensity connecting two coupled spins), the through-space distance between two spin nuclei can be estimated.

279 POPULATION TRANSFER APPLIED TO THE INDIRECT OBSERVATION OF NUCLEAR SPINS WITH LARGE QUADRUPOLE COUPLING CONSTANTS. **Alexander J. Vega[1] and Clare P. Grey[2], [1]DuPont Central Research and Development, P. O. Box 80356, Wilmington, Delaware 19880-0356; department of Chemistry, State University of New York, Stony Brook, NY 11794-3400.**

Although the satellite transitions of half-integer quadrupolar nuclei are typically too broad for detection by NMR, they can have an indirect effect on the observable spectra of the central transition of the same nucleus or on the spectra of dipolar-coupled neighboring spins. Suppression or modification of these interactions by application of conventional rf pulse methods to the broad transitions is impractical. However, the quadrupolar spins can often be manipulated by inducing population transfer among their energy levels. Various aspects and MAS applications of this approach will be reviewed, including its implications for CPMAS of quadrupolar nuclei, the establishment of spacial correlations between neighboring spins, the measuring of interatomic distances, and the determination of large quadrupole-coupling constants.

SURFACES, SOLIDS AND GASES: THE PHASES OF NMR SPECTROSCOPY, Cecil Dybowski, Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716.

NMR techniques for examining the nature of materials are explored, with examples from work at the University of Delaware. Surface structures are defined through analysis of dipolar couplings of ^{13}C and ^{1}H spins in adsorbed molecules; lineshape changes generated by motion give clues to the nature of site exchange in a catalyst; the spectroscopy of adsorbed gases gives insight into interactions of these molecules with the adsorbent. Comparison with gas-phase measurements using drift tubes and mass spectrometry indicate that, in some cases, the interactions of gas molecules with ions in adsorbents may be similar to interactions in the gas phase probed by these techniques.

281 INTERMEDIATE RANGE ORDER IN GLASSES: A NEW FRONTIER FOR SOLID STATE NMR SPECTROSCOPY. **Hellmut Eckert. Department of Chemistry, University of California, Santa Barbara, CA 93106**

Nuclear magnetic resonance in combination with magic angle spinning has contributed immensely to a detailed understanding of nearest-neighbor correlations in amorphous materials. This success is largely based on satisfactory chemical shift discrimination between sites having differing coordination numbers and/or ligands. Such a kind of analysis is, however, only a first step towards understanding an amorphous structure. Recent efforts have increasingly focused on order/disorder phenomena on larger length scales (5-15 A), which are thought to play a decisive role in the structural control of thermal and mechanical properties of glasses. Because NMR chemical shifts are generally not sensitive enough to probe such "intermediate range order", dipolar solid state NMR approaches such as spin echo, MAS- spin diffusion, SEDOR, REDOR, and other heteronuclear X-Y double resonance NMR techniques are becoming increasingly important tools for studying such effects. In addition, high-temperature liquid state NMR studies of the corresponding molten systems provide unique thermodynamic information on various speciation equilibria, reaction enthalpies and reaction entropies. Based on such experimental approaches, the structure of Phosphorus-Selenium based binary and ternary glass systems is discussed in detail.

282 SPINS, LIGHT, MOLECULES, AND CATS, Alexander Pines, Lawrence Berkeley Laboratory and University of California, Berkeley.

As a tribute to A. J. Vega, I shall outline some geometric aspects of spin dynamics and show how recent work of Aharonov, Berry, Wilczek.et al. has provided a unification of apparently disparate areas of physics and chemistry. I shall describe in simple, pictorial terms the similarity of the gauge potential in phenomena involving coherence and phase of spins in NMR and optics, fractional quantum numbers in Jahn-Teller molecules, quantum projection, and the reorientation of cats.

283 PROTON AND ^{13}C NMR CHARACTERIZATION OF MORPHOLOGY AND DYNAMICS OF POLYMER BLENDS. Jolanta M. Snowel' and Joel B. Miller, Code 6122, Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5342.

The thermodynamic miscibility of the polymer blend of poly(vinylethylene) (PVE) and cis-1,4-polyisoprene (PIP) has been confirmed by calorimetry and thermal expansivity measurements. However, the unusually broad glass transition extending over 30K prompted further studies. Earlier carbon NMR results on this blend are interpreted as evidence for a heterogeneity of motional dynamics. Our present research is focused on elucidation of the nature of molecular motions ongoing in the temperature range below and above glass transition in the blends and also in the pure polymers. Motions on the order of the chemical shift differences or dipolar interactions modify powder patterns thus providing information about motional rates. Using the separated local fields (SLF) experiments we efficiently separate the dipolar couplings from the chemical shifts; the experimental data are next compared with simulated patterns. The one- and two- dimensional NMR techniques that we employ include cross polarization (CP), magic angle spinning (MAS) and multiple-pulse decoupling. Spectral editing methods are also used to observe signals in the spectral regions with overlapping resonances.

* NRC/NRL postdoctoral associate

284 HIGH RESOLUTION NMR OF SOME QUADRUPOLAR NUCLEI IN THE SOLID STATE. B. C. Gerstein, Ames Laboratory, USDOE, 229 Spedding Hall, ISU, Ames, IA 50011-3020

A recently developed two-dimensional experiment promises high resolution solid state NMR of some quadrupolar nuclei. The concepts behind the idea will be explained, and, if available, experimental results on model compounds presented.

285 ANALYSIS OF ELECTRIC FIELD GRADIENTS AND ELECTRONIC SHIELDING BY SIMULATION OF SPINNING SIDEBAND INTENSITIES IN M.A.S. NMR SPECTRA. P. Bodart, C. Fernandez and J.P. Amoureux, LDSMM, Universite des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq (France).

The theoretical description of the effects on quadrupolar nuclei of a simultaneous presence of Chemical Shift Anisotropy (CSA) and Electric Field Gradients (EFG) with a possible disorientation of their Principal Axis Systems (PAS) is reported for Static, Magic Angle Spinning (MAS), Variable Angle Spinning (VAS), and OOuble Rotation (DOR)NMR powder spectra. The results show that an accurate determination of CSA and EFG parameters is possible by a precise analysis of the powder spectra, only if the disorientation of these interactiogytensorsris considered even for rotating samples. The experimental study of the Rb and V MAS spectra at various fields of various rubidium salts and of vanadium coumpounds provides a good illustration of such a potentiality.

Simulations of the spectra have been carried out by taking into account the CSA and quadrupolar interactions at the first or second-order and the disorientation of their PAS. This allows the accurate determination of the quadrupolar constant for each crystal!ographic sites present in the structure of the differents compounds.

286 **PROGRESS in NMR SPECTROELECTROCHEMISTRY, Krzysztof Franaszczuk, Andrzei Wieckowski. and Bernard Montez, Eric Oldfield, Department of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Mathews Ave, Urbana, IL 61801-3792, USA**

Recent progress in solid-state NMR measurements with l^C-enriched adsorbates, surface CO and CN, at the metal/solution interfaces will be reported. We will focus on strategies used for electrode surface preparation, that allow for a sufficient rf penetration through reducing "skin effects". We will show NMR results obtained under electrode potential control. Using cyanide adsorbed on a platinum electrode, we will demonstrate the effect of temperature on 13 C lineshapes and relaxation in the range of 10 to 300 K. Since the applicability of a Korringa relation for the cyanide adsorbate implies that the Pt-CN bond has substantial metallic character, relating the conduction electron density on the interfacial nuclei to the nature of the electrode materials, types of adsorbates and electrolyte can, in the long run, create a novel data base for understanding subtle, subatomic features of the double layer structure. That is, it may provide a missing element in the total definition of the electrified, solid/liquid interface.

287 **TEMPERATURE-JUMP MAS EXPERIMENTS WITH A LASER HEATER David Ferguson, Tom Krawietz and J. F. Haw. Department of Chemistry, Texas A&M University, College Station, TX 77843.**

We report the design and application of an MAS probe with an 80-wt C02 laser heater. This system allows us to jump the sample temperature at a rate of 300° per second in order to examine chemical reactions on a short time scale. Fairly rapid drops in temperature permit a "T-jump and quench" experiment Very high maximum temperatures are routinely achievable with this device.

Experimental design considerations include rotor material choice and thickness, sample length, etc. Some of these effects will eventually be modeled to get a better handle on temperature and temperature gradients (spatial and temporal). Applications will include reactions on catalysts, thermal decomposition reactions, and problems in mineralogy and glass chemistry.

288 RECONSIDERATION OF THEORY OF PARAMAGNETIC SHIFT FOR NI(II) AND C0(II) IN OCTAHEDRAL AND TETRAHEDRAL SYMMETRIES. Bruce R. McGarvey, Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, N9B 3P4, Canada

The theory of the paramagnetic shift in octahedral and tetrahedral complexes of both Ni(II) and Co(II) complexes has been re-examined after the discovery of some errors in earlier treatments. PC computer programs were then written to calculate both the pseudo contact and Fermi terms. The results will be presented and applied to literature data. One interesting theoretical result is the non-isotropic Fermi contact shifts for distorted tetralehal (Ni(II) and octahedral Co(II) complexes resulting from the strong spin-orbit contributions the ground state in these systems.

289 **^{31}P NMR STUDY OF THE REACTION OF PMe3 WITH $Mo(CO)_6$ IN Y ZEOLITE,**

Sanlin Hu and Tom Apple, Chemistry Department, Rensselaer Polytechnic Institute, Troy, NY 12180

The reaction of molybdenumhexacarbonyl with trimethylphosphine in dyhydrated NaY zeolite has been studied by ^{31}P solid-state NMR spectroscopy. The overall rate of the reaction is governed by the two-term rate law:

$$\text{rate} = \text{IqrMoCCO)}^{\wedge} + k_2[Mo(CO)_6][PMe3]$$

The reaction changes from a predominantly SN_2 mechanism in the temperature range from 298 K to about 338 K to an SN_1 mechanism at higher temperatures. $Mo(CO)_5PMe3$ is the major product of the substitution reaction, but some $Mo(CO)_4(PMe3)_2$ is also formed at the higher temperatures. Negative entropies of transition ($AS^{\ddagger}$) in the low temperature region and positive $AS^{\ddagger}$ values at high temperatures are consistent with the proposed mechanisms. The reaction is activated by the a-cages of NaY zeolite via a lowering of the enthalpy of transition ($AH^{\ddagger}$) allowing the reaction to proceed even at room temperature, unlike the behavior found in decalin solvent in which temperatures above 373 K are required.

290 COMPARISON OF THE SOLUTION CONFORMATION AND HISTIDINE PKA'S OF b-AMYLOID PEPTIDE FRAGMENTS. Cvnthia K. Larive and Shana L. Zink, Department of Chemistry and Center for Bioanalytical Research, University of Kansas, Lawrence, KS 66045

The peptide **B**-amyloid **(1-40)** has been reported to be the major protein constituent of the plaque formed in Alzheimer's patients. We have examined the conformation of two synthetic fragments of this peptide, **B**-amyloid **(1-28)** and **(12-28)** in **60%** Trifluoroethanol (TFE) / **40%** aqueous solution using two-dimensional NMR spectroscopy and circular dichroism. Both of these peptides adopt similar helical conformations in low pH solutions as evidenced by the cross peaks in the NOESY spectra of these peptides. The conformation of these peptides is known to be pH dependent. At low pH the peptides assume a helical structure, at intermediate pH they exist predominantly in the p-sheet conformation, and at high pH, a helical conformation is again favored. The pKa's of the histidine residues of the peptides have been determined by measuring NMR spectra as a function of solution pH. The pH of the mixed TFE/**H2O** and **d3TFE/D20** solutions used in this work were calibrated from the pH meter readings of known buffer mixtures in these solvents. The protonation/deprotonation of histidine residues of the peptides probably play an important role in the pH dependent conformational equilibria observed for these peptides.

291 **FREQUENCY-SELECTIVE OBSERVATION OF WEAK HETERONUCLEAR DIPOLAR COUPLINGS IN SOLIDS**

Andrew E. Bennett, Lino R. Becerra, and Robert G. Griffin
Francis Bitter National Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

In solid state nuclear magnetic resonance spectroscopy, several methods have recently been introduced for the purpose of restoring dipolar couplings into magic angle spinning experiments. These powerful techniques are useful for the measurement of internuclear distances and, more generally, for filtering and correlation experiments in non-crystalline materials. In the case of heteronuclear spins, the Rotational Echo Double Resonance experiment provides an elegant and practical approach to the spectrally non-selective reintroduction of dipolar interactions. We describe an approach to restoring heteronuclear couplings which is spectrally selective - in particular, the observed spins are recoupled only with those non-observed spins lying at exact resonance (and at multiples of the spinning speed) in a triple resonance experiment. We refer to the technique as Frequency-Selective Dipolar Recoupling (FDR). In addition, the potential for adapting this approach to static solids is discussed.

292 **THE USE OF ^{13}C CHEMICAL SHIFT TENSORS TO STUDY CRYSTALLINE EFFECTS IN POLYCYCLIC AROMATIC HYDROCARBONS.** **R. J. Iuliucci. Cu Phung, Julio C. Facelli and David M. Grant, Department of Chemistry, University of Utah, Salt Lake City, UT 84112**

The sensitivity of nuclear shielding on the local electronic environment of the nuclei as well as the large anisotropic nature of ^{13}C chemical shift tensors provides a means to probe crystalline effects. The inherit advantages of 2D chemical shift - chemical shift correlation spectroscopy utilizing our flipper probe extends chemical shift tensor studies to complex crystal systems such as polycyclic aromatic hydrocarbons. The unit cell of acenaphthene contains two crystallographically different molecules. The overall chemical shift distance between the corresponding molecules of acenaphthene is 1.6 ppm which is significant compared to the uncertainty in the determined chemical shift tensors of 0.4 ppm. In solid phase naphthalene and perylene, the chemically related nuclei within the molecules are exposed to different crystalline environments. The deformations to these crystallographically nonequivalent nuclei are evident by shift distances between these related tensors which exceed by several fold the experimental errors in the tensor measurements. The changes in the chemical shift tensor are indicative of variations in the molecular structure. The influence of subtle changes in bond angles and lengths, including the consequence of breaking of the planar symmetry on the chemical shift tensor will be addressed.

293 **^{6}Li NMR CHEMICAL SHIFTS AND Li COORDINATION IN LITHIUM SiLICATES AND ALUMINOSILICATES** **Z. Xu and JF.Stebbins, Deptof Geology, Stanford University, Stanford, CA 94305.**

Lithium is a difficult nucleus for x-ray diffraction due to its small number of electrons. Also for the same reason the chemical shift range of lithium NMR spectra is usually very small. However, °Li nuclide has a small quadrupolar coupling constant (50 times smaller than that of ^{7}Li) and low natural abundance (about 4%), which will cause very small dipole-dipole interactions. These two features of ^{6}Li nuclide make it possible for us to obtain high resolution solid state NMR spectra. In this study we have collected °Li magic angle spinning (MAS) NMR spectra on a number of lithium silicates and aluminosilicates, including LUSiCH (lithium orthosilicate), Li2Si205 (lithium disilicate), K(Li,Al)2-3(AlSi30io)(0,OH,F)2 (lepidolite), (Be,Li)3A12(Si60io) (beryl), Li(AlSiOin) (petalite), LiAlSi2Si6 (spodumene), LiAl4(AlSi30io)(OH)8 (cookeite), LiAlSi04 (eucryptite). Our data suggest that ^{6}Li chemical shift correlates well with the Li-0 coordination environment and is not sensitive to the Al/Si ratio. The chemical shifts of three-, four-, five- and six-coordinated Li atoms fall into the range of 1.5 to 1.4 ppm, 0.9 to 0.7 ppm, 0.2 to 0.0 ppm and -0.6 to -1.0 ppm, respectively. For lithium orthosilicate, which is known from previous single crystal x-ray diffraction study to contain three-, four-, five- and six-coordinated Li atoms, results of 2D homonuclear correlation spectroscopy (COSY) show the presences of cross-peaks between three- and four-, four- and five-, four- and six-coordinated Li atoms, which indicates the connectivities among these Li sites. We have also found that °Li enriched sample (95% °Li) and the sample of the natural abundance ^Li have identical linewidths for all the four different Li coordination environments. Thus, we think the cross-peaks observed are probably due ot J-coupling between the correspinding Li coordination environments.

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Abstract Not Available

295 **THE CHARACTERIZATION OF LEWIS ACIDITY AND SURFACE ALUMINUM IN VARIOUS ALUMINAS AND ZEOLITES BY MEANS OF HIGH RESOLUTION MAS AND CP/MAS ^{27}Al AND ^{15}N NMR.** **Alexander Blumenfeld, Dominique Coster, and Jose J. Fripiat, Department of Chemistry and Laboratory for Surface Studies, PO Box 413, University of Wiscosin-Milwaukee, Milwaukee, WI, 53201.**

Although local surrounding and bonding of acid active sites on a catalyst surface has a profound effect on the NMR spectral features (chemical shifts, line widths, quadrupolar parameters), it is difficult to get unambiguous structure-spectral assignments from conventional ^Al NMR spectra even under high speed MAS conditions. This is mainly because of the poor spectral resolution caused by broad distributions of local electronic surroundings and electric field gradients in disordered catalyst structures and also by residual second-order quadrupolar broadening. Though some promising quantitative results were reported recently on model well-crystalline materials, little progress has been achieved so far with real catalysts under conditions close to those occurring in practice. It is a purpose of this work to study the nature of Lewis acidity in various active catalysts (aluminas and zeolites) pre-treated under controlled atmosphere at different temperatures. Isotopically enriched ammonia $^{15}NH_3$ chemisorption was employed to probe the surface active sites and to allow for magnetization transfer from protons to surface and close-to-surface Al nuclei. A special deconvolution procedure was developed and applied to obtain ^{27}Al spectral parameters for different $^{27}A1$ sites in partially resolved spectra . The procedure accounted for the normal distribution of EFG tensor components at a particular site. As a result we were able to characterize on alumina surfaces and in zeolites two kinds of Lewis sites originating from tetrahedral Al^ and pentahedral Al^.

296 PROBING ELECTRONIC STRUCTURE IN $M_2Mo_6Se_6$: QUADRUPOLE COUPLINGS MEASURED BY NMR.

David B. Zax, Benjamin G. M. Chew, Josh H. Golden, and Francis J. DiSalvo,
Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853.

Novel electronic properties are often associated with low-dimensional systems. We have been probing electronic structure in a variety of systems M2Mo6Se6, where M = Li, Rb, Cs or In. These highly anisotropic systems are composed of polymeric $(Mo_3Se_3)_n$ chains separated by columns of metal (M) cations. Changing the cation has a profound impact on the electronic properties. Where M=In or Tl, the resistivity varies with temperature like common transition metals with delocalized conduction bands. Where M is an alkali metal, the electronic state at low temperature is semiconducting, from which we infer that the conduction Hand is localized on individual chains. We have investigated this difference via measurements of the electric field gradients at the cations, probed via nuclear magnetic resonance. These values are compared to values calculated for an ionic lattice based on the x-ray-derived lattice. The measured values deviate significantly from calculation only for M=In. This deviation is attributed to partial In p-orbital contribution to the conduction band, which would provide a mechanism for the interchain electronic coupling observed in I^MogSeg.

297 Measurement of ^{13}C-^{13}C Distances in DNA using Radio Frequency-driven Dipolar Recoupling NMR

***David Gregory, Dan Mitchell, Jerome Shiels, and Gary Drobny**
Departments of Chemistry and Physics, University of Washington, Seattle, WA 98195

Local Structure and motion in DNA is of vital importance in understanding the interaction between DNA and proteins. We have used Radio Frequency-driven Dipolar Recoupling (RFDR) NMR to determine C- C distances within spinning samples of DNA. We will demonstrate how these give us insight into the relative orientations of adjacent bases in DNA. Numerical simulations, using density matrix formalism and finite pulse widths, of these spinning experiments will be shown to support the experimental distance measurements.[1-3] I I C- C distance measurements are also determined for model compounds to further support the DNA measurements. These simulations and experimental results will be used to address the robustness of these RFDR NMR distance measurements when the chemical shift Lnisotropies of both ^{13}C spins are large. The use of multiple quantum MAS experiments for structure determination will also be investigated.

298 High Frequency (13 9.5 GHz) Dynamic Nuclear Polarization Solid State NMR (DNP-SSNMR)

Lino R. Becerra[1] Gary J. Gerfen[1] Brendan F. Bellew,[1] Dennis A. Hall,[1] Richard J. Temkin,[2] David J. Singed Robert G. Griffin.[1]
[1] Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139.
[2]Plasma Fusion Center, Massachusetts Institute of Technology, Cambridge, MA 02139.
•^Department of Chemistry, Harvard University, Cambridge, MA 02138.

DNP-SSNMR experiments at high frequency (139.5 GHz, 5 Tesla, 211 MHz proton Larmor frequency) have achieved significant nuclear polarization enhancements in the 150 K to 20 K temperature range. Proton signal enhancements of greater than 60 have been obtained in static samples of the free radical BDPA doped into polystyrene (PS) using cylindrical resonators to increase the intensity of the driving microwave field. The technique has been applied to other paramagnet/solvent systems in order to study aspects of the DNP mechanisms. These systems include BDPA (small g-anisotropy) in frozen toluene, galvinoxyl (relatively large g-anisotropy) in frozen toluene, chromium (V) (large g-anisotropy) in watenalcohol, and nitroxides (large g-anisotropy, large hyperfine coupling) in watenalcohol. The temperature, power, and field dependence of DNP enhancements is discussed. Extension of these techniques to magic angle spinning experiments is presented.

299 **SOLID STATE NMR STUDIES OF SELF-ASSEMBLED MONOLAYERS (SAMs).** Glen E. Fryxell, Li-Qiong Wang, John C. Linehan and Peter C. Rieke. Battelle, Pacific Northwest Laboratories, P. O. Box 999, Richland, Washington, 99352.

Several solid state NMR techniques have been employed to characterize terminally derivatized SAMs. Methods used include 1H CRAMPS, 13C CP-MAS and Bloch decay and 29Si CP-MAS and Bloch decay. These techniques have provided key insight into the binding, cross-linkling and loading density of these monolayer systems. We have successfully monitored chemical change taking place at the interface between the monolayer and the underlying substrate, as well as functional group transformations at the alkyl chain terminus. These methods have also provided the first accurate demographics of crosslinking and surface attachment.

300 **VARIABLE EFFECTIVE FIELD CROSS-POLARIZATION: AN APPROACH TO BROADBAND HARTMANN-HAHN MATCHING IN MAGIC-ANGLE SPINNING NMR.** **Andrew C. Kolbert and Sheryl L. Gann. Materials Sciences Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California** 94720.

A method for broadening the Hartmann-Hahn matching condition for cross-polarization under magic angle spinning is presented. Variable effective-field cross-polarization (VEFCP) employs different effective radio-frequency (r.f.) fields on the 'H channel during mixing, while the ^C r.f. field remains constant. The effective r.f. fields are generated by using successive time-averaged-precession-frequency (TAPF) pulse sequences during the mixing time. The TAPF pulse sequence consists of a y-pulse of duration *t_c-t,* followed by a -y-pulse of duration T. Provided that *t_c* is small compared to the dipolar correlation time of the protons in the solid, the TAPF sequence results in a net nutation about the y-axis at an effective r.f. field of amplitude *(t_c-2x)C0]/t_c.* By combining successive TAPF sequences with differing values of T, varying effective fields are created during the contact time which serve to broaden the matching conditions and average the kinetics of the polarization transfer. VEFCP is shown to result in both a broader matching condition and a more rapid polarization transfer than ordinary cross-polarization. Experimental results on both adamantane and polycarbonate are presented.

301 **VARIABLE-TEMPERATURE ^{13}C CP/MAS NMR STUDY OF FLUXIONAL BEHAVIOR OF Cp_4M (M=Zr, Hf, Sn) IN THE SOLID STATE** **Eric J. Munsonf. Susan M. DePault, Marcia A. Ziegeweidt, Leo Phillips*, Frances Separovic*, and Alex Pines, ^Materials Sciences Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, CA 94720 and ^Department of Biochemistry, University of Sydney, NSW 2006, Australia**

Variable-temperature ^{13}C CP/MAS NMR has been used to study the fluxional behavior of cyclopentadienyl-containing organometallic complexes with the formula Cp_4M (M=Zr, Hf, Sn). The X-ray structure of these compounds has shown that these molecules contain both *monohapto-* (n,^{1}-C5H5) and *pentahapto-* (r^-CsHs) cyclopentadienyl groups. Results will be shown in which lineshape analysis has been used to monitor the sigmatropic rearrangement of the (r^-CsHs) groups in (rj^1-C5H5)20l^5-C5H5)2Hf in the temperature range of 173-273 K, from which was calculated Arrhenius activation parameters. Two-dimensional exchange results will be presented that have been used to attempt to distinguish between [1,2] and [1,3] shifts. Results of similar experiments performed on the (r|^1-C5H5)i(r|^5-C5H5)3Zr and (r ^ ^ H s ^ S n complexes will also be presented.

302 **31p NMR OF ZnGeP2: AN OPTICAL PARAMETRIC OSCILLATOR.** **Margaret H. Rakowsky and Robert A. Mantz, The Frank J. Seiler Research Laboratory, USAF Academy, CO 80840-6272 and Phillips Laboratory, Edwards AFB, 93524-7068.**

Zinc germanium phosphide is a semi-insulating ternary chalcopyrite used as a nonlinear optical material for second harmonic generation and as an optical parametric oscillator in tunable lasers. However, its use has been limited to the mid-IR region by an optical absorption shoulder in the 0.7-2.5 p.m region. Improvement in the optical properties of crystalline ZnGeP2 correlates with a decrease in the number of defects seen by electron paramagnetic resonance in several samples. In this study, we have examined the 3 lp magic angle spinning nuclear magnetic resonance of five samples of either polycrystalline or single-crystal ZnGeP2- Using NMR we determined if the chemical shifts were the same for each sample, if there was evidence of different crystallographic phases, and if the anisotropy was the same for each. The results of this study and the correlation of the data with optical and EPR data will be presented.

303 **MAGNETIC EFFECTS IN BIMOLECULAR REACTIONS OF ION-RADICALS IN SOLUTIONS.** Nikolai V.Shokhirev, University of Arizona, Tucson, Arizona 85721; Anatoli A.Zharikov, Institute of Chemical Kinetics and Combustion, Novosibirsk, 630090, Russia; Eugeni B.Krissiriel', Institute for Water and Environmental Problems, Barnaul, 656099, Russia.

Flash-CIDNP has become a powerful method for the investigation of recombination and charge transfer processes as well as the reaction mechanisms. To interpret such experiments, it is necessary to know the bimolecular rate constants of the reactions that yield products in certain nuclear configurations and electron spin multiplicity. Using the analytical approximation of the Green function for diffusion motion in the Coulomb potential, we derived general expressions for rate constants of bimolecular reactions of charged particles in solvents of arbitrary polarity. The case of contact recombination with the step-wise exchange interaction was considered. In the case of high magnetic fields and primary unpolarized radicals, the general expressions reduce to simple analytical formulae for the stationary rate constants. A comparison of the analytical and precise numerical calculations shows good accuracy of the proposed approach. Also discussed are the non-trivial influence of solvent polarity and viscosity on rate constants via singlet-triplet conversion efficiency, and the violation of simple sign rules.

304 **CHARACTERIZATION OF GASOLINE ENGINE COMBUSTION CHAMBER, INTAKE VALVE, AND CRANKCASE DEPOSITS BY SOLID-STATE ^{13}C CP/MAS NMR SPECTROSCOPY**
John C. Edwards, Texaco Research Center, P.O. Box 509, Beacon, New York, 12508

Solid-state ^{13}C NMR spectroscopy has been used to study the carbonaceous deposits generated in the combustion chambers and crankcases of dynamometer test - engines. Combustion chamber and intake valve deposits, in particular, have been identified as having detrimental effects on vehicle driveability and emissions performance. The combination of cross-polarization and dipolar dephasing techniques was used to determine the "average molecule" parameters of these deposits. These parameters were then used to correlate the deposit structure with gasoline composition and cylinder cleanliness. The "average molecular structure" of the deposits from different engine types, and from different locations in the engine, will be discussed. Analogies with the "average molecular structures" of other complex "carbonaceous polymers", such as coal and asphaltenes, will be presented. Finally, we will demonstrate how this NMR deposit analysis can be used to develop bench tests which effectively simulate the combustion environments in automotive engines.

MEASURING VARIABLE-TEMPERATURE PERFORMANCE OF MAS PROBES

Anthony Bielecki and Douglas P. Burum, Bruker Instruments, Inc., Billerica, MA 01821

The MAS spectrum of ^{207}Pb in solid lead nitrate exhibits a remarkable temperature sensitivity. Over at least the range of -100 to +140 °C, the chemical shift varies linearly, within experimental error, with a slope of 0.753 ± 0.004 ppm/°C. Also, its natural linewidth is small (< 0.5 ppm) and its NMR sensitivity is relatively high. This combination of properties makes lead nitrate an excellent practical standard for measuring temperature changes and temperature gradients in MAS probes.

Lead nitrate is a strong oxidizer. Do not mix it into other samples.

Since lead nitrate has only one ^{207}Pb resonance, it cannot by itself be used to determine the absolute temperature. However, observation of melting points of known standards can accomplish this. This allows for the measurement of temperature sensor errors, either due to electronic artifacts or temperature gradients along the probe air stream.

306 OLEFIN ROTATION DYNAMICS OF RHODIUM COMPLEXES. **Greta L. Garner. Les G. Butler, Stephanie A. Vierkotter, and Craig E. Barnes, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, and Department of Chemistry, University of Tennessee, Knoxville, TN 37996.**

Molecular motion of monomeric and dimeric rhodium olefin complexes in the solid state from 260 K to 370 K has been studied by a combination of ^{1}H, ^{2}H, and ^{13}C solid-state NMR. In the complex $Rh(acac)(C2D_4)_2$, the ^{13}C spectra shows coalescence of crystallographically inequivalent carbon sites, the Tip shows a minimum value at temperature later found to correspond to an olefin motion on the order of $5x10^{4}$ s^{-1}, and the ^{2}H line shape undergoes a characteristic line shape change at a rate of $2x10^{4}$ s^{-1}. Analysis of the ^{2}H data is made somewhat difficult since a 180° olefin rotation transfers deuterons among magnetically equivalent sites, assuming a planar olefin unit. Fortunately, olefins coordinated to metals often exhibit hydrogen "bend back" and are nonplanar. The complex Rh(acac){C2D4)2 has a bend back angle of 12°, thus enabling a line shape analysis of the ^{2}H NMR spectra.

307 FIELD CYCLING ^{14}N NQR IMAGING AND SPECTROSCOPY. **Youngil Lee and Les G. Butler, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803**

The recently developed technique of NQR imaging via field cycling has been used to image 1^N nuclei in a test sample of acetamide and salicylamide. The image obtained is spatially resolved in one dimension and is also obtained as a function of the I0> —» I+> transition frequency. The imaging plane is generated by two collinear solenoids wound with opposite handedness. In the field cycling experiment, the 1 I0> —> I+> transition, is saturated throughout the sample except at the imaging plane where the magnitude of the rf field, IB11, is near zero.

A field cycling NQR spectrometer has been developed based on an MSL200, a high speed linear stepping motor, and an Oxford gas flow cryostat. The linear motor can operate in the fringe field of the 4.7 T magnet; the linear motor has important advantages over previous shuttle systems based on pneumatic devices (variable positions and speed). The variable position is frequently used to select an advantageous magnetic field for polarizing the proton spin system.

308 SOLID STATE ^{19}F-^{13}C CP/MAS "C NMR STUDY OF POLYFLUORINATED C_{60}.

E. W. Hagaman and A. Gakh, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6201

Recently there has been considerable interest in preparing and characterizing highly fluorinated fullerenes (see Cox, D. M. et.al. *J. Am. Chem. Soc.* 1994,*116*, 1115-1120, and references therein). In connection with this effort we have examined several $C_{60}F_x$ samples by ^{19}F-^{13}C CP/MAS ^{13}C NMR. Preparations of highly fluorinated buckyball (C_{60}) contain a sharp set of resonances we assign to $C_{60}F_{46}$ and a second component observable as a broad resonance (90-140 ppm) peaked at 118 ppm, the chemical shift region of gemmaZ-difluorocarbon resonances. This resonance is clear evidence for rupture of the ball. Irrespective of the detailed structure of this broken polyfluorinated buckyball, the molecule will no longer possess the nearly spherical structure of $C_{60}F_{46}$, and a significant difference in molecular reorientation time between these components should exist. We use this difference to separate the components, spectroscopically, using either the ^{19}F-^{13}C dipolar dephasing time, T_{DD}, or the ^{19}F T^. Both relaxation times are long for the plastic crystal component, C_6oF_{46}, relative to that for the broken polyfluorinated buckyball.

309 SCOTCH TAPE, CAPILLARY TUBING, AND SUPERGLUE: HIGH PRESSURE NMR. **John C. Linehan, Clement R. Yonker, James A. Franz, and Thomas S. Zemanian, Pacific Northwest Laboratory, P.O. Box 999, Richland WA, 99352.**

High pressure, high resolution ^{1}H, ^{19}F, ^{129}Xe, and ^{13}C NMR spectra have been collected on fluids and compressed gasses in a new capillary NMR vessel which fits inside of standard NMR tubes and standard- liquid NMR probes. The new high pressure vessel is inexpensive (<$10 per cell), safe (fails at >60,000 psi), and is easy to use. We present isotherms of NMR spectra collected on compressed gasses and supercritical fluids (ethylene, propane, methane, sulfur hexafluoride, and xenon) as well as organometallic species in solution equilibrium with high pressure gasses. The new high pressure vessel, which is composed of multiple bends of GC quality fused silica capillary tubing, can be easily spun to yield high resolution proton spectra or used for flow through applications.

Work supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. CRY acknowledges the support of the Advanced Processing Technology Initiative.

310 13c CPMAS AND ROTATIONAL ECHO NMR STUDIES AND X-RAY CRYSTALLOGRAPHY OF BIS-PHENOLS AND POLYCARBONATES. **J. B. Grutzner. B. Cowans, and Y.-H. Lee, Departments of Chemistry and Chemical Engineering, Purdue University, West Lafayette, IN 47907-1393.**

A series of bis-phenols and polycarbonates have been studied by l^C CPMAS and rotational echo NMR spectroscopy and x-ray crystallography. The monomers have been studied as crystals and glasses and the polycarbonates as glasses. The importance of x-ray crystallography for interpreting CP-MAS NMR spectra will be illustrated. In the crystal, the phenyl groups adopt two conformations - the eclipsed with the vicinal alkyl group generating a chiral conformer, or the bisected geometry which has a plane of symmetry. NMR studies alone would have led to an incorrect assignment. In the glassy state both monomers and polymers have a distribution of phenyl orientations.

The dynamics of phenyl motion in glassy samples have been studied by rotational echo CP-MAS spectroscopy with a series of 180° pulses synchronized with the rotor frequency echo. Broad lines arising from static magnetic and sample inhomogeneities are refocussed into a series of sharp lines with homogeneous linewidths. The echo spectra give improved signal/noise and confirm that line broadening in the CP-MAS spectra arises from static local fields rather than molecular motion. The effect of molecular structure on dynamics will be discussed.

Abstract Not Available

2 **MOLECULAR DYNAMICS OF SEMIS YNTHETIC CYTOCHROME C: Implications For Electron Transfer**

* **Sheri A. Hunt, Regitze R. Void, Ph.D. and David N. Hendrickson, Ph.D.**
Department of Chemistry, University of California, La Jolla, CA 92093.

One of the central challenges in molecular biophysics is to understand how proteins control biochemical reactions in living organisms. A goal is to develop a tool that will allow us to understand the biomolecular structure and dynamics of an electron transfer protein and how they are responsible for the unique capabilities of this protein. To understand how energy is stored and utilized requires that the mechanisms for bioenergetic electron transfer be understood. The main focus of most studies of electron transfer reactions has so far been to investigate how the rate depends on distance. This study is focused on the molecular dynamics of relevant amino acid residues in order to answer questions about the possible gating effects on biological electron transfer rates. The principal tool of study is solid state deuterium NMR spectroscopy. This work makes extensive use of experimental techniques, NMR lineshape simulations, and relaxation rate measurements. The single peptide chain of horse heart cytochrome c, an electron transfer protein, contains two methionine residues. One of these, in position 80, is coordinated to the heme iron and is of major importance for the molecule while the one in position 65 is arranged on the surface. The cleavage of the molecule with cyanogen bromide, which cleaves specifically on the carboxy terminus side of methionine residues, yields a heme peptide and two nonheme peptides. Semisythethic cytochrome c consists of coupling this 65 residue heme peptide with a synthetically generated 39 residue peptide. Two semisynthetic horse heart cytochrome c's were prepared, each with a singly substituted deuterated amino acid, the methionine methyl, position 80, in one and the five ring positions of phenylalanine position 82 in the other. The symmetry, amplitude and rates of motion were determined for these selectively deuterated amino acids in the 39-mer as well as in the semisynthetic cytochrome c.

312 MULTI-MAGNETIC RESONANCE STUDIES OF NOX REDUCTION CATALYSTS.

Craig D. Hughes and William L. Earl, Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545

We have been working on the problem of the catalysis of the reduction of nitrogen oxides in automotive exhaust. The best catalyst for the *proposed "lean* burn" *technology is a copper exchanged* ZSM-5 zeolite. The mechanism of action of this catalyst is poorly understood. We are applying a multitude of magnetic resonance techniques to this problem. These include ^N, 27Al, ^{29}Si, and 63QI NMR studies as well as ESR. We will discuss the results of our efforts to characterize the catalyst starting material, our results in characterizing the catalyst after exposure to realistic operating conditions, and our conclusions about how the structure affects the performance of the catalyst. We will also present results on several other zeolites including structural and prehminary catalytic results.

313 ADVANCES IN UNDERSTANDING ^{129}XE NMR IN RESTRICTED SPACES.

Yong-Wah Kim and William L. Earl, Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545

After several years of experimentation on a large number of different systems we finally understand the qualitative aspects of ^{129}Xe chemical shifts in porous materials. There are shift effects due to the extrinsic properties of the particles. These have been discussed in some detail by Ripmeester and co-workers. Once these are accounted for, there are affects due to the chemical nature of the pore and due to the dimensions of the pore. We will demonstrate the NMR apparatus used to investigate these phenomena over a wide temperature range as well as a wide xenon loading. We will discuss the qualitative aspects of the effects of the pore wall and present our data on the effects of temperature on both the adsorption and the ^{129}Xe chemical shift. Our results extend the utility of ^{129}Xe NMR for the study of pore size and structure but do not put this technique in the realm of routine pore characterization by the uninitiated. We will discuss the advantages and pitfalls of ^{129}Xe NMR compared to other pore characterization methods.

i4 **RECENT DEVELOPMENTS IN DISTANCE MEASUREMENT TECHNIQUES FOR SOLID STATE DNA SAMPLES.** **John A. Stringer , Jon Callahan and Gary P. Drobny University of Washington, Seattle WA. 98195.**

Solid state spin 1/2 spectra are dominated by nuclear chemical shift anisotropics (CSA) whose removal requires averaging through the use of magic angle spinning. Unfortunately sample spinning also removes the dipolar coupling interaction which contains the distance information of interest Application of radio frequency pulse sequences in synchrony with the sample rotation reinstates the dipolar coupling while not affecting the CSA averaging. New results regarding the design and application of such "sequences will be presented along with recent developments in 13c-19p and 19p_19p distance techniques. Specific applications to nucleic acids will be considered.

315 **SOLID STATE ^{13}C NMR STRUCTURAL STUDIES OF AN INTERCALATING DRUG BOUND TO DNA.** **Suzanne R. Kiihne, Gary P. Drobny, University of Washington, Seattle, WA 98107.**

Intercalation complexes of small drugs with DNA helices have significant biochemical and medical importance, but do not yet have experimentally well defined structures. Study of these complexes in the dry and hydrated non-crystalline states accessible to solid state NMR provides a solution to many of the experimental problems which have plagued previous X-ray crystallography and high resolution NMR studies. A variety of solid state NMR techniques have been applied to ^{13}C-proflavin.HCl and to its intercalation complex with calf thymus DNA. Magic angle spinning (MAS) techniques have been combined with total sideband suppression (TOSS) to average the chemical shift anisotropics and simplify the spectra. Relaxation studies have shown a close association of the drug and DNA molecules. Application has also been made of new double quantum filtering (DQF) techniques which provide unique information about the structural environment of the ^{13}C label through a dependence on dipolar interactions containing both distance and orientation information. Signal to noise ratios and filtering efficiencies have been somewhat improved in the double quantum methods by incorporation of TOSS techniques. This last combination has allowed the observation of correlations between the ^{13}C label of the drug and surrounding sites containing ^{13}C at natural abundance.

316 **NMR, MRI, AND TUMOR FORMATION.** **Rodolfo A. Santos. Breege A. Concannon*, Darrell R. Fisher, Kevin M. Groch and Robert A. Wind, Pacific Northwest Laboratory, P. O. Box 999 Richland, WA 99352. *Dept. of Chem. and Biochem., University of South Carolina, Columbia, SC 29208.**

It has been known for a long time that some NMR parameters such as the proton T_1 and T_2 are different in healthy and tumorous tissues. At Pacific Northwest Laboratory a research program has been started to investigate whether additional NMR parameters are sensitive to tumor formation; whether NMR and MRI can be used to differentiate between healthy, preneoplastic, and neoplastic lesions; and whether this can be achieved in the early stages of the various transformation. To this end a multinuclear, multifield, multitemperature NMR/MRI investigation has been initiated of rat mammary, liver, and lung tissues and cells obtained after exposure of the animals to carcinogenic chemicals or radiation. We will examine which NMR parameters are the most sensitive to the tumor formation, and use pattern recognition techniques to optimize the characterization of the various stages. One of the goals of this study is to determine accurate dose-response curves, which are of critical importance with respect to the cleanup of radioactive and toxic waste at the U.S. Department of Energy's Hanford site and at other sites. First results of the research will be presented.

Pacific Northwest Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76-RLO 1830.

317 **ELECTRON SPIN ECHO SPECTROSCOPY OF GAMMA-IRRADIATED QUARTZ.** **V.V. Kurchev* and H.A. Buckmaster**. *Department of Chemistry, University of Houston, Houston, TX 77204-5641, USA. **Department of Electrical and Computer Engineering, University of Victoria, P.O. Box 3055, Victoria, B.C., V8W 3P6, Canada.**

Gamma-irradiated fused quartz has been investigated at 290 K using 1.7 and 9.8 GHz electron spin echo spectroscopy. Three-pulse stimulated echo sequences were used in this study because the observed modulation effects were very small using two-pulse echo sequences. It was found that no electron echo envelope modulation could be observed at 9.8 GHz but that a small relative amplitude envelope modulation signal could be observed at 1.7 GHz if the time interval between the first and second pulses was 1.0 or 3.0 |is but not for 2.0 u,s. It was concluded that this modulation is due to the magnetic dipole interaction between the E^-centres and ^{29}Si nuclei. The natural abundance of this isotope of silicon is 4.7%, 1=1/2 and |i=-0.5553 u.$_n$. Unsuccessful attempts were made to model this modulation signal assuming that the Ej-centre was located at oxygen and silicon vacancies in the hexagonal lattice of quartz. It was concluded that the E_1 -centre behaves as if it does not interact with the nearest or next nearest neighbour ^{29}Si nuclei. Acceptable agreement was obtained if this electron centre is located at a silicon vacancy and only interacts with all nuclei located outside a 0.5 nm radius sphere. This implies that the point charge model may not be applicable because the electron appears to be delocalized within this spherical volume.

318 **PHASE-CYCLED, MULTIPLE-WINDOW-ACQUISITION, MULTIPLE-PULSE NMR SPECTROSCOPY** **Thomas Barbara and Laima Baltusis.Varian NMR Instrument Division, 3120 Hansen Way, Palo Alto, CA 94304.**

Quadrature-corrected data for the solid-state homonuclear decoupling sequences MREV8, BR24, and CORY24 are obtained, using a new method that combines experiments from a set of properly chosen preparation pulses. This method is compared to the usual approach that requires sampling in more than one data window per cycle. An overview of the data available in all large windows for these sequences is presented.

319 **INVESTIGATION OF THE INTERFACIAL STRUCTURE OF POLYPHOSPHAZENE-PHOSPHATE MOLLUECULAR COMPOSITES USING ^{31}P-S0LID NMR.** **William D. Samuels, Li-Qiong Wang, and Gregory J. Exarhos, Pacific Northwest Laboratory, MS; K2-44, Richland, WA 99352. Alma R. Rodriquez, UTEP, Student Internship at Pacific Northwest Liboratory, MS; K2-44, Richland, WA 99352.**

Solid NMR spectroscopy has been applied to changes in structure of inorganic polymer/phosphate glass composites. Single Pulse Block Decay, CP-MAS, and CRAMPS techniques have been use to study the interfacial structures. Strong interfacial bonding between the component phases is also inferred from electron micrographs. Mutual solubility of inorganic polymers, typified by the polyphosphazene, -[N=PR$_2$J-$_x$ and metal phosphate glasses in a solvent such as water allows intimate mixing on the molecular scale. Solvent evaporation followed by thermal processing generates material having nanoscale microstructure which can be modified by appropriate choice of processing parameters.

320 **SOLID-STATE NMR STUDIES OF HYDROXYL GROUPS IN DEALUMINATED USY ZEOLITES.**

Edward F. Rakiewicz, Alan W. Peters, W.R. Grace and Co.-Conn., 7379 Rt. 32, Columbia, MD 21044, Karl T. Mueller, Dept. of Chemistry, Penn State University, University Park, PA 16802

Zeolites are microcrystalline aluminosilicates that are used in several important commercial applications such as ion-exchangers and catalysts. Due primarily to their commercial importance, a significant amount of effort has been put forth to better understand the relationship between these materials' structure and performance properties. In many of these studies, solid-state NMR has provided valuable insight into their structure of these materials that could not be obtained.by. any other technique. In particular, NMR has been shown to be an especially useful method to study the structural changes that occur upon removal of aluminum atoms from the zeolite framework. Starting with a template synthesized Y-zeolite (Si/AI=4.1), we have been using solid-state ^{1}H-^{29}Si cross-polarization (CP) NMR to determine the structural changes that occur after removal of some framework aluminum by a mild (530°C, 2 hours) steam treatment. Our results Show that, in addition to the formation of the previously assigned mono-silanol $(SiO)_3SiOH$ signal at -100 ppm, we also observe signal enhancements of the -95 and -90 ppm resonances in the CP spectrum compared to one-pulse experiments. Using chemical shift arguments and the results of a ^{27}Al-^{29}Si dipolar dephasing solid-state NMR experiment, we propose that a portion of these signal intensities are due to previously unobserved framework silanol sites $(SiO)_{3-x}(OAl)_xSiOH$ where x= 1 and 2, respectively. The unique structure of these sites suggests that they may be play an important role in the acid catalyzed reactions that occur in the zeolite pores.

*' **DYNAMICS OF METHANE AND ETHYLENE MOLECULES ON SILICA SUPPORT**

Son-Jong Hwang*»2. jj# c. Gerstein^, a n r j Marek Pruski^.
^Department of Chemistry and ^Ames Laboratory, Iowa State University, Ames, IA 50011.

l^C MAS NMR and 2D exchange NMR were employed to investigate the dynamics of small hydrocarbon molecules such as methane and ethylene on the silica support (Cab-O-Sil HS 5). Molecules adsorbed on the siiica surface and in the gas phase were observed as two distinct peaks in the MAS NMR spectra. Changes in chemical shift and the amount of molecules in the two phases were studied under different pressures and in the temperature range from 170 K to 370 K. The exchange process between these phases were measured using the selective spin population inversion method. The exchange rate was extremely slow.

322 **LINE BROADENING AND RELAXATION IN MOLECULES ADSORBED IN FAUJASITES - A CASE STUDY OF 1-BUTENE**

Uwe Schwerk and Marek Pruski,
Ames Laboratory, 230 Spedding Hall, Ames, IA 50011

The influence of the adsorbent on NMR linewidhts and relaxation is examined using proton MAS NMR for 1-butene adsorbed on faujasite type zeolites. Line broadening is shown to depend on the size of zeolite crystallites and the amount of paramagnetic impurities in the zeolite lattice, while restricted mobility of the molecule has negligable impact at room temperature. Small amounts of molecular oxygene impurities in the adsorbed gas do not affect resolution, but may result in increased longitudinal relaxation. Unusually high resolution can be observed in favourable cases, allowing the detection of J coupling between protons.

423 QUALITY CONTROL IN PARAMETER-SELECTIVE IMAGE ANALYSIS

Richard Miffler, Peter Barth, and Winfried Kuhn. Fraunhofer Institut fur Bioniedizinische Technik, Ensheimer Str. 48,66386 St. Ingbert, Germany

Parameter-selective imaging has been shown to be a valuable tool for the investigation of materials as well as for biological applications. From a series of differently weighted NMR images it is possible to calculate NMR-parameters such as relaxation times Tl, T2, Tip or diffusion constants. Furthermore the estimation of parameters, which describe directly material properties is done on the basis of physical models. In order to quantify the quality of the parameter selective images obtained from NMR-measurements, we developed a software package with different validation possibilities of the images. This package works in the software environment SUNRISE. We use only quality control methods which are independent of the physical Model used to obtain the parameter selective image. The tools are based on advanced Nonlinear Regression Methods. The following *tools* are used for quality control:

- **Calculation of a modell-check image**
- **Variation coefficient images for each parameter**
- **Histogram analysis for a region of interest**
- **Plot of normalized residuals for single pixels or a region of interest**
- **Calculation of confidence intervals for each parameter in a single pixel**

This quality-monitoring possibilities allow to draw conclusions about the reliability of the estimated NMR-narameters and of the derived material properties. The software package is very helpful to find systematic errors and can also be used to optimize the experimental parameters.

323 SOLID-STATE NMR STUDIES OF ISOLATED TWO-SPIN SYSTEMS INVOLVING NITROGEN: DIAZO COMPOUNDS.

Robin Challoner and Robin K. Harris. Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England. Phone (+44)-91-374-3121, FAX (+44)-91-386-1127.

In principle, solid-state NMR gives a wealth of detail about nuclear magnetic interactions and about molecular geometry. The most favourable case is that of isolated spin pairs, yet suitable systems are rare. However, the diazo group provides a classic case, which also allows an increased number of experiments because of the existence of two magnetic isotopes of nitrogen, 1^N(I=1) and l^N^—)- We have studied sodium 5-methyl-2-diazobenzene sulfonate, using samples enriched in ^N at each position and at both sites together. Rotational resonance MAS and off-angle spinning *^{15}N spectra have been used for the ^{15}N2 sample. Static and MAS spectra have been obtained for the a-^N and p-^{15}N cases. MAS spectra show effects of residual ^{15}N,^{14}N dipolar interactions. Analysis of all the experiments produces information on shielding tensor components, quadrupolar coupling constants and internuclear distances.

324 NUCLEAR QUADRUPOLE RESONANCE (NQR) STUDIES OF GLASS STRUCTURE

Philip J. Bray, Department of Physics, Brown University, Providence, RI 02912, USA

Nuclear Quadrupole Resonance (NQR) studies have been reported previously from this laboratory for the case of boron (the ^{11}B and ^{10}B nuclear isotopes) in borate glasses. The work has now been extended to NQR studies of aluminum (using the ^{27}Al nuclear isotope) in glasses containing aluminum oxide (AI203). Examples to be discussed include glasses in the system AI203— Te02 and vitreous anorthite (CaO • AI203 • 2Si02). Work is also in progress on ^{51}V NQR studies of vanadate glasses, with, vitreous potassium vanadate as the initial example. NQR spectra often reveal sites in both glasses and polycrystalline powders that are not detected by NMR since all of the structured NMR responses overlap around the Larmot frequency. Vitreous boron oxide (-B203) and borogermanate glasses are interesting examples whose ^{11}B NQR spectra will be discussed. NMR studies of alkali ions in glasses indicate that the distributions of environments are generally very broad, making it difficult or impossible to detect NQR spectra. The NQR work employs a modified Robinson-type regenerative oscillator that functions well at quite low frequencies. Current studies are detecting resonances in the 250 kHz to several MHz range.

325 FIELD SWEPT NMR SPECTROSCOPY: APPLICATIONS TO ZEOLITES. **Xiao Wu and Les G. Butler. Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803**

A field-swept NMR spectrometer has been constructed based on an Oxford 16/18 Tesla (4.2/2 K operation) superconducting magnet. Spectra are acquired point-wise with a either long-duration, small tip angle RF pulse or a spin-echo sequence. The apparatus has been tested with ^{27}Al and ^{23}Na NMR of OC-AI203, a single crystal of andalusite, and several zeolites. Effective spectral widths of up to 8 MHz have been employed (andalusite). Spectra are acquired with a sample temperature of 4.2 K (immersed in He). A new $^{27}A1$ NMR resonance is found in a high Si/Al hydrogen faujasite that is assigned to a nonframework site.

326 HIGH FREQUENCY DYNAMIC NUCLEAR POLARIZATION and ELECTRON PARAMAGNETIC RESONANCE **L. R. Becerra[a], G. Gerfen", J. Bryanr[3], B. F. Bellew*, D. Hall* S. Inati[a], K. J. Kreischer^, R. J. Temkin*>, D. J. Singel[c] and R. G. Griffin^** *[a]Francis Bitter National Magnet Laboratory, Department of Chemistry, [b]Plamsa Fusion Center, MLT,Cambridge, MA 02139 [c]Department of Chemistry, Harvard University, Cambridge, MA 02138*

Signal-to-noise (S/N) in high resolution solid state NMR experiments can be enhanced with dynamic nuclear polarization (DNP) techniques involving irradiation of the EPR spectrum of paramagnetic samples with microwaves. DNP has been performed successfully at frequencies £ 40 GHz for e"'s (60 MHz for ^{1}H), and in favorable cases enhancements range from -20-250. However, because of the absence of high power microwave sources operating at > 40 GHz, these experiments have not been executed at the higher fields commonly employed to enhance sensitivity and resolution in NMR exr^riments. Recently, we have developed the necessary instrumentation to extend DNP experiments to higher frequencies. First, we have assembled a 140 GHz pulsed and CW EPR spectrometer, since it is important to know the shape of the EPR spectrum as well as the relaxation times of the associated paramagnetic center. Second, we have constructed a CW gyrotron - a high frequency, high power microwave oscillator - operating at 140 GHz (210 MHz for *H) and incorporated it into a DNP/NMR spectrometer. The design and operation of this device in pulsed and CW mode will be discussed, results ulusrrating DNP enhanced NMR spectra will be presented, and the possible extension of these techniques to higher operating frequencies will also be considered.

327 PULSED ENDOR SPECTROSCOPY OF ^{57}Fe CONTAINING ZEOLITES. **D. Goldfarb+. M. Bernardo, K.G. Strohmaier and D.E.W. Vaughan, Exxon Research and Engineering Co.; Route 22 East, Clinton Township; Annandale, NJ 08801**

The catalytic properties of zeolites can be modified by variations of the zeolite composition such as the incorporation of Fe^{3+} into tetrahedral (T) framework sites. The EPR spectra of such materials usually reveal several types of Fe^{3+} signals indicating the coexistence of both framework and non framework iron. The assignment of the signals is, however, most often ambiguous. In order to obtain a better characterization of the Fe^{3+} sites pulsed electron-nuclear double resonance (ENDOR) experiments on ^{57}Fe enriched zeolites were carried out. The latter provides the NMR spectrum of the ^{57}Fe from which the hyperfine coupling is readily obtained. Moreover, the NMR spectrum can resolve Fe^{3+} sites with overlapping EPR signals. Pulsed ENDOR measurements were performed on ^{57}Fe-Sodalite which is unique in the sense that its EPR spectrum is characteristic of a single species assigned to framework T sites. Therefore it can serve as a reference for T sites in zeolites. The peaks observed were assigned using hyperfine selective ENDOR experiments and orientation selective experiments. The effect of the zero field splitting on the ENDOR spectra , the use of pulse ENDOR in the investigation of the synthesis mechanism of &Fe-Sodalite and spectra obtained from other zeolites will be discussed as well.

"•"Permanent address: Chemical Physics Department, Weizmann Institute of Science, Rehovot 76100, Israel

328 DYNAMIC NUCLEAR POLARIZATION OF CONTAINING FREE RADICALS.

Richard D. Bates. Jr.. Department of Chemistry, Georgetown University, Washington, DC 20057.

An overview of the contributions of dynamic nuclear polarization (DNP) to studies of interactions of solvent species and paramagnetic probes in solution will be presented. Measurements will be compared with studies of the same systems by other magnetic resonance methods. Low field DNP investigations of nuclei interacting in solution with free radicals have provided important information about electronic structure of the two species by identifying the relative contributions of scalar and dipolar coupling of the nuclear and unpaired electron spins. The paramagnetic-species induced component of the relaxation of solvent nuclei provides complementary information by acting as a sensitive probe of the molecular motions of the interacting nuclear and unpaired electron spin. Separation of the dipolar contribution arising from rotation of the transient complex from the translational diffusion of the species free in solution has been achieved by varying the solvent composition with an inert cosolvent. Current investigations of solvent-solute interactions between proton donors and nitroxide radicals examine the dynamics of short-lived complex formation on the molecular level by a range of magnetic resonance approaches.

329 A ^9Si DYNAMIC NUCLEAR POLARIZATION/MAGIC ANGLE SPINNING STUDY OF THE SILIC/ SURFACE.

Jun.ji Kobayashi, Materials and Electronic Devices laboratory, Mitsubishi Electric Corp., Hyogo 662, JAPAN

^{29}Si direct polarization spectra of the silica surface have been selectively observed via dynamic nuclear polarization (DNP) combined with magic angle spinning(MAS). The DNP enhancement of a nuclear polarization has not been reported so far on any surface species. We could observe the enhancement of at least a factor of 50 on ^9Si solid NMR spectra. The dehydrated silica surfaces were coveraged with approximately 0.53(monolayer BDPA free radicals. The electron polarization was transferred directly via DNE to the ^aSi spin system. No enhancement has been obtained with the electron spin polarization transferring to the proton spin system. The samples above-mentioned were outgassed to 10"^ Torr because the spin lattice relaxation rate of the unpaired electron of BDPA is needed to be as long as possible. The depth of enhanced regions of ^{29}Si polarization was deeper via the DNP ..transfer from the electron spin system than via the cross polarization transfer from H nuclear spin system. In addtion, the signals due to surface species such as (HO)Si (OSi)$_3$, (HO)oSi (OSi)$_2$ were more enhanced than that due to the bulk silicon (Si (OSi)$_4$). I woulcr like to thank Prof.Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-0002.

330 ADVANCES IN HIGH-FREQUENCY, PULSED EPR/ENDOR SPECTROSCOPY

J. Schmidt Huygens Laboratory, University of Leiden, P.O. Box 9504, 2300 RA Leiden, The Netherlands

The main incentives to develop EPR spectroscopy at mm wavelength are the high spectral resolution, resulting from differences in or anisotropy of the g-factors of the various paramagnetic species, and the high absolute sensitivity that can be achieved. The 95 GHz, pulsed EPR spectrometer which has been constructed at the University of Leiden fulfills this expectations. I will illustrate its performance by presenting the results of three experiments. The first concerns a study of the photo-induced, shallow electron center in AgCl, which is thought to be the precursor of the formation of the latent image. The high resolution is illustrated by the first observation of the complete ENDOR spectrum involving the ^{107}Ag, ^{m}Ag, ^{35}C1 and ^{37}C1 nuclei. The high absolute sensitivity is illustrated by the first observation of the EPR spectrum of the metastable triplet state of a minute single crystal of (dimensions 0.2 x 0.2 x 0.2 mm^3). Further I will present the first EPR spectrum of a single crystal of the blue-copper protein azurin. Here it proved possible to determine the principal axes of the g-tensor of all 16 sites in the unit cell. Recently we even succeeded in observing the ^{14}N ENDOR spectra.

331 **"Solid State NMR, Pulsed ENDOR, and Multiple Quantum Spectroscopic Studies of Interfaces in Fullerene Polymer Blends", M. Afeworki, M. Bernardo, and H. Thomann, Exxon Corporate Research Lab, Rt 22 E, Annandale, NJ 08801**

We have observed an increase in the thermally and mechanically measured glass transition temperature for elastomers solution blended with a few weight per cent fullerenes. In general, the modification of the viscoelastic properties of polymers is mediated through the interface between the dopant and polymer, particularly the molecular dynamics at the interface. We have taken advantage of two unique properties of the C60 molecule, its characteristic 13C resonance and its low reduction potential, to investigate the interface between the C60 molecule doped into polyisoprene and ethylene propylene copolymers using a variety of magentic resonance techniques. Results from variable temperature proton linewidth, 1H-13C cross polarization dynamics, selective cross polarization, pulsed EPR measurements of the C60 radical relaxation, EPR detected multiple quantum (MQ) NMR and MQ-ENDOR experiments will be presented.

332 **STRUCTURE AND DYNAMICS IN SOME LOW-DIMENSIONAL COMPOSITE PHASES. David B. Zax. Benjamin G. M. Chew, and Shan Wong, Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853.**

Low-dimensional phases are often associated with unusual electronic and/or mechanical properties. We have recently been studying several low-dimensional systems composed of blends of inorganic and organic phases. As interesting macroscopic properties are generally associated with either structural or dynamic aspects of the blends (or both), our work has focused on understanding how parameters observable via nuclear magnetic resonance reflect these features of the local environment. The chemistry in our systems leads us to focus primarily on exploiting quadrupole coupling constants, both in the inorganic layers (where our probes are most often alkali metals), and in various organic polymers (where ^{2}D is a more useful probe), in addition, to whatever spin-1/2 nuclei are convenient. Our measurements have shed light on the electronic properties of some inorganic conducting polymers, and have revealed unusual dynamic effects in polymers confined in two dimensions.

333 **MULTI-NUCLEAR NMR STUDIES OF ZEOLITE FERRIERITE. [a]Lucy M. Bull.[a]Scott J. Weigel,[b]Michael T. Janicke and [a]Anthony K. Cheetham,[a]Materials Research Laboratory and [b]Chemical Engineering Department, University of California, Santa Barbara, CA 93106. U.S.A.**

Interest in the structure and properties of the aluminosilicate form of ferrierite has recently been stimulated by a report that it is an excellent shape-selective catalyst for the isomerization of n-butenes to isobutene (J. Haggin, C. and E. News, Oct. 25, 30 (1993)). The structure of the calcined siliceous ferrierite has been determined from a combined analysis of synchrotron X-ray and neutron powder diffraction data. The *Vmnn* space group with which the structure was refined, requires five crystallographically distinct Si sites. The 29si MAS NMR spectrum of siliceous ferrerite can be resolved into five resonances, which can be fitted quantitatively to the site multiplicities if the linewidths are allowed to vary. The bond lengths and bond angles for each Si site have been correlated with the ^{29}Si NMR chemical shifts, and with information obtained from 2D NMR experiments, COSY and INADEQUATE, the ^{29}Si NMR spectrum has been assigned. 29si MAS NMR spectra of high aluminum content ferrierite structures (Si/Al=8 and 6) have been simulated from the siliceous spectrum assuming; 1) a random distribution of Al, 2) each aluminum substitution in the first T-site coordination sphere shifts the resonance down field by 4.5 ppm, and 3) gaussian lineshapes of width 400 Hz.

334 PROTON AND ^{19}F NMR OF SOLED THIN FILMS AND INTERFACES. David H. Levy, Bruce E. Scruggs, and Karen K. Gleason. Department of Chemical Engineering, M.I.T., Cambridge, Massachusetts 02139.

The inherent low sensitivity of NMR makes the study of solid thin films and interfaces challenging. Hydrogen is an ubiquitous impurity in such environments, either as an undesirable contaminant or as intentional component, introduced to passivate defects. In order to detect low *H concentrations, an NMR probe was designed to accept stacks of silicon wafer slivers, providing > 100 cm^2 of single crystalline surface area per sample. No NMR sample tube is required, further eliminating background ^1H signals, allowing as few as 3.5x10*6 protons/solid sample, corresponding to nearly monolayer detection on a single crystal surface. These proton concentrations can be difficult, if not impossible, to measure by other techniques. This probe was used to obtain *H NMR spectra of hydrogenated defects in silicon dioxide films. This probe can also be used for multiple-pulse studies such as quadrature-detected, multiple-window sampling BR-24 *H NMR of silicon nitride thin films and multiple-quantum NMR studies of hydrogenated defects in chemically vapor deposited diamond films. The high-gyromagnetic ratio of and its isotropic chemical shift range also are desirable for surface studies. Surface coverages as low as 7.4 x 10*3 F/cm^2 were detected on diamond powder surfaces after treatment in a CF4 radio frequency plasma. High-speed magic-angle spinning resolved the presence of CF, CF2 and CF3 functionalities.

335 CONNECTIVITIES FROM NMR SPECTROSCOPY OF SOLIDS. APPLICATIONS TO MATERIALS RESEARCH. Karl T. Mueller and Thomas P. Jarvie, Department of Chemistry, Penn State University, University Park, PA 16802.

We are applying single- and double-resonance NMR techniques to study microstructural composition and structure in materials. One- and two-dimensional cross-polarization experiments, SEDOR, REDOR, TEDOR and related techniques are useful for probing inorganic solids such as zeolites, clays, and glasses where spectral features provide specific information from the bulk of the material. We are also probing interactions with reactive species at the interfaces of materials. The spectral editing features of many double-resonance techniques are particularly useful and have been exploited for probing local spin interactions.

336 Dynamics of Surface Adsorbed Polymers.. Frank D. Blum, Department of Chemistry and Materials Research Center, University of Missouri-Rolla, Rolla, MO 65401.

We have used both 13c and ^2H NMR to probe the mobility of various polymers on silica. In dispersions, the styrene segments of a partially deuterated block copolymer of styrene and 2-vinylpyridine, attached on silica and swollen in toluene, were found move faster than in the corresponding solutions. This phenomena dependent on the solvent quality. In poor solvents, such as carbon tetrachloride, the reverse trend was found. For poly(/so-propyl acrylate) on silica in the dry state, the surface was observed to change the nature of the polymer from rubbery to glassy at room temperature. This change in dynamics was also observed to be most dramatic at low coverages. For polyvinyl acetate)-d3 on silica, the glass transition temperature of the polymer, as observed by NMR, was found to increase in the presence of the surface. In addition, it was found that the glass transition occurs over a much wider temperature range on the surface than in bulk.

337 **NEW DEVELOPMENTS IN NMR STUDIES OF SOLIDS AND SURFACES**

Eric I. Munsont, Dinh M. TonThat*, Marcia A. Ziegeweidt, YiQiao Songt, Bin Het, Tanja Petrasst, Holly Gaedet, Rebecca Taylort, John Clarke*, and Alex Pinest, ttMaterials Sciences Division, Lawrence Berkeley Laboratory, ^Department of Physics, and tDepartment of Chemistry, University of California, Berkeley, CA 94720

Some of the new developments in the areas of optical pumping and low frequency NMR will be described. Optical pumping can be used generate large polarizations of ^{129}Xe magnetization. The highly polarized ^{129}Xe is then used to probe surfaces and porous materials. Recent advances in the transfer of magnetization from optically polarized ^{129}Xe to other nuclei will be shown. A low frequency pulsed NMR spectrometer has been developed that uses a DC Superconducting QUantum Interference Device (SQUID) as a flux to voltage converter. This spectrometer can be used to observe NMR and NQR resonances in the 0-1 MHz frequency range. Details of the construction of this spectrometer will be presented. One of the problems associated with low frequency NMR is the weak signal due to the small population difference between states. Techniques will be shown that can be used to increase the population difference and enhance the sensitivity of the experiment.

338 **INTERMEDIATE-RANGE STRUCTURAL INHOMOGENEITIES IN GLASSES: A NUCLEAR SPIN-LATTICE RELAXATION APPROACH.** **S.Sen and LF.Stebbins, Deptof Geology, Stanford University, Stanford, CA 94305.**

Intermediate-range ordering beyond next nearest neighbors in depolymerized silicate glasses/melts can be induced by clustering of the constituent structural units. Nuclear spin-lattice relaxation, when dominated by the fluctuation of dipolar coupling between the nuclei and unpaired electrons in paramagnetic dopants, has been found to be a sensitive indicator of the spatial distribution and clustering of both the paramagnetic ions and the nuclide under observation. Detailed ^{29}Si spin-lattice relaxation measurements in optically homogeneous Li2Si409 glasses doped with Gd203 (a paramagnetic dopant) show strong differential relaxation of the constituent Q^3 and Q^4 species. Faster relaxation of the Q^3 species indicate presence of Q^3 and Q^4 rich, nm sized clusters in the structure, with preferential concentration of Gd ions in the former. ^6Li spin-lattice relaxation also shows presence of fast and slow relaxing components which corroborates with the previous results. In the case of a homogeneous distribution of the paramagnetic ions, the spin-lattice relaxation rate, $Ti \sim (Np)^{-4/3}$ where Np is the number of paramagnetic ions. Deviations from this scaling relation in ^{29}Si spin-lattice relaxation have been used to study inhomogeneity in the spatial distribution of high field strength, Nd cations present in 600 to 2400 ppm concentrations in pure Si02 glasses. Our results indicate that once the clustering of Nd atoms starts, total number of clusters remain essentially constant, only the size of the clusters increases on increasing Nd concentration. These phenomena associated with paramagnetic induced spin-lattice relaxation can be useful in future for exploring inhomogeneities in structural randomness in amorphous materials.

339 **14N-!H LEVEL CROSSING IN IMMOBILIZED PROTEINS,** **SCOTT D. SWANSON.** ***Department of Radiology, The University of Michigan, Ann Arbor, MI 48109-0553***

A sample-shuttle NMRD (SSNMRD) spectrometer, constructed in this laboratory, has been used to study the ^{14}N relaxation peaks present in proton NMRD profiles of immobilized proteins. These relaxation peaks are created by magnetic cross-relaxation between the solvent protons, protein protons, and protein nitrogens when the proton energy-level splittings, due to the Zeeman interaction, are equal to the nitrogen energy-level splittings, due to the nitrogen quadrupole coupling constant (NQCC).

The frequencies of the two peaks present at about 2.2 and 2.8 MHz determine the average magnitude, e^2Qq/h, and asymmetry parameter, $r\backslash$, of the NQCC. Preliminary studies reveal that for bovine serum albumin (BSA), $e^2Qq/h = 3.301 \pm 0.0041$ MHz and $n = 0.401 \pm 0.0042$ while for hen egg white lysozyme (HEWL), $e^2Qq/h = 3.217 \pm 0.0046$ MHz and $n = 0.433 \pm 0.0049$.

In addition, we are interested in determining the sources of broadening of the ^{14}N peaks and extracting any information about the structure and/or dynamics of the proteins which these peaks may contain.

CROSS POLARIZATION DOUBLE ROTATION NMR.

Y. Wu. W. Sun, J. T. Stephen, and L. D. Potter. Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255

Spin locking and cross polarization of half-integer quadrupolar nuclei were investigated under double rotation (DOR). It was found that the efficiency of spin locking under DOR can be improved dramatically under weak spin-locking rf fields. This agrees qualitatively with the behavior of spin locking under MAS in the rapid passage regime[l j. The influence of DOR motion on the transfer rate of cross polarization (CP) and the matching condition were also investigated. Preliminary experimental results show that an efficient transfer of polarization under DOR occurs over a broad range of rf field amplitudes away from the Hartmann-Hahn matching condition. This range is even broader than the one under static condition without significant oscillations of transfer rate. Spectra of CPDOR can be easily obtained even with very weak dipole-dipole interactions of the protons. Applications of CPDOR in various molecular sieves will be demonstrated. The proximity between guest molecules absorbed by the molecular sieve and the host lattice can be revealed clearly by CPDOR.

[1] A. J. Vega, *J. Magn. Reson.* 96, 50 (1992).
[2] Y. Wu, D. Lewis, J. S. Frye, A. R. Palmer, and R. A. Wind, *J. Magn. Reson.* 100, 425 (1992).

^{31}P-^{19}F ROTATIONAL-ECHO, DOUBLE-RESONANCE (REDOR) NMR.

Yong Pan. The Procter & Gamble Company, Miami Valley Laboratories, P. O. Box 398707, Cincinnati, OH 4523'

Rotational-Echo, Double-Resonance 0*EDOR) NMR has been a very useful technique for retrieving information on weak heteronuclear dipolar coupling in the presence of large chemical-sbift anisotropics. ^{13}C-^{15}N, ^{13}C-^{31}P, and ^{13}C-^{19}F REDOR NMR techniques have been developed and applied to the study of various biological systems and polymeric materials. Recently, we extended REDOR to ^{31}P-^{19}F spin pairs for proton-absent or proton-dilute inorganic systems. The advantages of ^{31}P-^{19}F REDOR are that 1) both ^{19}F and ^{31}P have almost 100% natural abundance, so that specific isotopic labeling is not needed, 2) ^{19}F and ^{31}P also have large gyromagnetic ratios, allowing a greater range of measurable distances, 3) the high natural abundance and large gyromagnetic ratios result in high NMR sensitivity, and 4) for proton-absent or proton-dilute inorganic systems, ^{31}P-^{19}F REDOR can be performed on a routine two-channel NMR spectrometer. We used 31p.19p redOR to measure the nearest P-F distance in fluorapatite matrix. The 3.58 A distance obtained by NMR is in good agreement with 3.60 A obtained from X-ray diffraction. The application on fluoride-treated hydroxyapatite, the principal inorganic constituent of dental enamel and dentine, showed the formation of fluorohydroxyapatite with a coverage less than one layer of unit cell on the surface.

342 **MULTIPLE QUANTUM FILTRATION AND TRANSFER TO HETERONUCLEI ASSIGNS RARE-SPIN SIGNALS.** **Raju Subramanian and Gerard S. Harbison. Department of Chemistry, University of Nebraska at Lincoln, Lincoln, NE 68588-0304.**

Assignment of CP-MAS spectra, particularly those of ^{13}C in organic solids, is one of the major unsolved problems in solid state NMR. Until now there has been no general method for distmguishing between carbons of the same class and protonation state, save by selective isotope labeling. Our new method exploits the fact that the proton distribution in most materials is not isotropic, but clustered. Methylenes and methyls, for example, are two and three spin groupings with unusually large proton-proton dipolar couplings; in most organic molecules there are generally other useful short proton-proton contacts. Multiple quantum coherence within the proton spin system therefore develops rather unevenly. We exploit this unevenness by applying a standard 90° - x - 90° sequence to select for some order of coherence, typically double-quantum. This coherence is then immediately converted back to antiphase single quantum coherence via another 90° pulse, and, following a delay, transferred selectively to the rare spin, for example by using a very short period of Hartmann-Hahn matching. The result is a spectrum where the protonated carbons which cross-polarize from clusters of protons are enhanced. While the enhancements are usually not large, by comparing them with calculations we can use them to assign the carbon spectrum. This allows us to assign even carbons which are chemically equivalent in solution to unique sites in the crystal lattice.

343 **HIGH RESOLUTION NMR OF SINGLE EPITAXIAL STRUCTURES BY OPTICAL DETECTION,** **John A. Marohn. Paul J. Carson, Michael A. Miller, Jack Y. Hwang, David N. Shykind, and Daniel P. Weitekamp, A. A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125**

High-resolution solid-state NMR is a valuable tool in the study of semiconductors, but conventional NMR is too insensitive to probe the approximately 10^{12} nuclei in a single epitaxial structure. The circular polarization of luminescence from gallium arsenide is known to be modulated by nuclear magnetization transverse to the coincident static magnetic field and optical detection axis. This mechanism (a Hanle effect due to the net hyperfine field of the nuclei) has been used previously in steady-state experiments to optically detect low-resolution NMR spectra and in pointwise time-sequenced experiments to record high-resolution NMR spectra. By introducing a spin-locked "reference" nuclear field during evolution of the "observed" nuclear field, we are now able to optically record NMR spectra in real time by monitoring luminescence polarization oscillating near the difference in Larmor frequencies. An analytical model and experimental results demonstrate that linear response is maintained with nuclear fields large compared to the static field. Using optical Larmor beat detection, we obtain order-of-magnitude resolution improvement over previous NMR techniques for studying single epitaxial structures.

344 **VAD0R : A NEW HIGH-RESOLUTION TECHNIQUE FOR QUADRUPOLAR NUCLEI.** **J.P. Amoureux C. Fernandez and P. Bodart, CNRS URA 801, Universite des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq (France).**

00R is a very powerful technique for solid-state analyses' of quadrupolar nuclei. However, in a few years, spectra recorded with this technique will be perfect examples of beautiful mirages :
*** BEAUTIFUL : At present the external-rotor spinning speed is limited to 1.5 KHz. In a few years, this speed will reach approximately 2.5 KHz, which implies 5KHz spaced sidebands for synchronized experiments. Therefore, on high field spectrometers, resonances of each species will consist of a narrow line, as in liquids.**
***MIRAGE : These narrow lines will appear far from the "correct" chemical shift consequently to the induced quadrupole shift (which is important if D0R is used).**

Therefore, we propose a new two-dimensional technique.(VAD0R : Variable Angle D0uble Rotation)), equivalent to VACSY for CSA (L. Frydman, G.C. Chingas, Y.K. Lee, P.J. Grandinetti, M.A. Eastman, G.A. Barrall and A. Pines, J. Chem. Phys., 97(7), 4800(1992), which simultaneously keeps the high resolution aspect and avoids the loss of the chemical shift.

424 **MEASUREMENT OF HYDROXYL RADICAL FORMATION USING MICRODIALYSIS SAMPLING & GCMS QUANTITATION.** AW Pike, PV Fennessey, JM McKim. Department of Pediatrics, University of Colorado School of Medicine, 4200 E. 9th Ave., Denver, CO, 80262. (303)270-7287.

By combining microdialysis (MD) and hydroxylation of salicylate (SA), with GCMS detection, a highly specific, and sensitive system for monitoring "OH formation has been developed. GCMS conditions for measuring SA and its hydroxy isomers (2"3- and 2'5 dihydroxybenzoic acid (DHBA) were determined using authentic standards. Separation of SA isomers and determination of retention times was achieved using a DB1 high resolution GC column. Mass spectra were obtained using electron impact conditions. The most intense ion, M-15, was used for selective ion monitoring. Samples and standards were spiked with 3-and 4-hydroxy benzoic acid as internal standards, extracted with ethyl acetate and derivatized with BSTFA. Simultaneous quantitation of SA, 2'3- and 2'5-DHBA was achieved using standard curves. MD conditions were established using a CMA-120 (10 mm tip) MD probe. Relative recoveries for each isomer ranged from 95% at 1 jjl/min to 30% at 10 /il/min at 25°C. The entire system was tested using a hypoxanthine/xanthine oxidase reaction containing iron, EDTA, and SA in PBS at pH 7.4 to generate "OH. Samples were collected at 5 min intervals for 30 min at 37°C. Conversion of SA to 2'3- and 2'5-DHBA by 'OH increased steadily over time. Reactions without xanthine oxidase showed no spontaneous conversion of SA. In the presence of desferal, vitamin E, and catalase "OH formation was greatly reduced or undetectable. (Supported by NIH-DK34914).

DEVELOPMENT, VALIDATION AND TRANSFER OF DISSOLUTION METHODS.
Diane L. Peterson and Michael J. Baltezor
Marion Merrell Dow, Inc., 10236 Marion Park Drive, Kansas City, MO 64137

In order to develop and validate a rugged dissolution method which can be easily transferred, it is important to have a good understanding of the theory of dissolution and the role of the key parameters. An overview of the theory of dissolution and the parameters to consider in developing dissolution methods is provided. The role of the physical and chemical properties of the drug substance, the dosage form characteristics, the selection of an appropriate dissolution apparatus, and the determination of key parameters are discussed. The validation of dissolution methods is discussed with an emphasis on the importance of ruggedness determinations. Practical approaches to dissolution method transfers are provided, along with examples of troubleshooting common problems.

346 **MICELLAR IMPROVED DETERMINATION OF 6-AMINOPENICILLANIC AND 7-AMINO-CEPHALOSPORANIC ACIDS.** Natalia Iatsimirskaia. Anatoly Yatsimirsky, and Iulia Sosnovskaya, Facultad de Quimica, Universidad Nacional Autonoma de Mexico (UNAM), Mexico D.F., 04510 Mexico

6-Aminopenicillanic (6-APA) and 7-aminocephalosporanic (7-ACA) acids are important intermediates in the synthesis of P-lactam antibiotics. A commonly used procedure for determination of 6-APA is />-dimethylamino-benzaldehyde (DAB) method based on the condensation of DAB with 6-APA affording colored Schiff base (^max^[15] nm). We found that the addition of sodium dodecylsulphate (SDS) greatly enhanced both the rate of formation and the yield of the product. At optimum SDS concentration (0.016 M) and optimum pH 2.3 the observed equilibrium constant of the reaction is ca. 100 times higher than that in pure aqueous solution. Under these conditions 3 mM concentration of DAB is sufficient for the complete convertion of 6-APA into the Schiff base and the limit of its determination is 1.0 ug/ml, that is ca. 50 times lower than in the absence of SDS. 6-ArninopenicilIoinic acid, the product of hydrolysis of the P-lactam ring of 6-APA, does not interfere with 6-APA determination. The method was for the first time applied for determination of 7-ACA. The reaction product had the absorption maximum at 423 nm. The optimum conditions, 0.022 M SDS and pH 2.3, were similar to those for 6-APA. The limit of determination of 7-ACA was 4.0 ug/ml. The micellar improved reaction was applied for the flow injection determination of 6-APA produced by enzymic hydrolysis of benzyl penicillin.

CHROMATOGRAPHY AS AN ANALYTICAL AND QUANTITATIVE TOOL FOR THE ISOLATION OF AN ANTI-CANCER DRUG, TAXOL FROM THE YEW SPECIES. Vishnu Vandana and Amyn S. Teja, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100.

Taxol, a naturally occurring diterpene alkaloid, has shown promise as an anticancer drug in the treatment of ovarian and breast cancer. There is a need for better separation methods to extract most of the drug from natural resources. In this study, a novel separation process has been developed to isolate taxol and related taxanes from *Taxus brevifolia.* The alkaloids are extracted from the plant material by supercritical fluid extractions and separated by chromatography. Two new post-extraction methods have also been developed. The first is an analytical method to identify taxol and other taxanes in the extracts qualitatively. The second method consists of a preparative scale separation of taxol and other desired compounds. The preparative method achieves better yields of taxol and does not involve the usage of FDA regulated halogenated solvents.

347 PROPOSED METHOD FOR THE ANALYSIS OF SOLVENT IMPURITIES IN WATER INSOLUBLE BULK PHARMACEUTICALS. **Valerie J. Naughton, Tekmar Company, 7143 East Kemper Road, Cincinnati, Ohio 45249**

The automated static headspace analysis of Organic Volatile Impurities (OVI's) in water soluble pharmaceutical bulks has been demonstrated (1). This method is applicable to approximately 60% of the drugs proposed for testing by the United States Pharmacopeia (USP). This paper is a proposed addition to Method IV (USP chapter (467)), addressing the analysis of OVI's in water insoluble pharmaceutical bulks. To analyze solvent impurities by static headspace analysis, the pharmaceutical material must be solvated. Those materials which are water soluble are amenable to static headspace analysis, because of the OVI's have relatively low partition coefficients in water. Water insoluble pharmaceutical materials pose a more difficult problem. These materials will readily dissolve in organic solvents, however the resulting partition coefficients for the OVI's prohibit static headspace analysis. Alternate sample dissolution techniques were investigated to enable the static headspace analysis of water insoluble pharmaceutical materials. This paper describes a technique which balances the solvating properties of strong organic solvents with the matrix modifying capability of saturated aqueous salt solutions. This balance permits pharmaceutical bulk solubilization and subsequent static headspace solvent impurity analysis. 1. K.J. Dennis, P.A. Joseph, J. Dokladova, "Proposed Automated Headspace Method for Organic Volatile Impurities (467) and Other Residual Solvents", Pharm. Forum, 1992 18(1), pp. 2964-2972.

348 CHARACTERIZATION OF TAXOL METABOLITES BY LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY.

Kelly R. Thornbura. and Robert C. Hyta, Hauser Chemical Research, 5555 Airport Road, Boulder, CO, 80301; Gondi N. Kumar, and Thomas Walle, Department of Pharmacology, Medical University of South Carolina, Charleston, SC 29425.

Taxol, an antimitotic agent derived from the Pacific yew tree, has been shown to be effective against a variety of cancers. Its metabolic fate is, however, incompletely understood. As most of the taxol dose is excreted in feces, it has been difficult to elucidate its metabolism *in vivo.* In recent *in vitro* studies in the rat we identified two aromatic hydroxylation products both in hepatocytes and in liver microsomes (Walle et al., Biochem Pharmacol 468:1661, 1993). The aliphatic hydroxylation product 6a-hydroxytaxol was identified as the main metabolite in human liver microsomes (Kumar et al., Drug Metab Dispos 22:177, 1994). In these studies the metabolites were identified after prior isolation and purification by HPLC. In the present study we report on line coupling of mass spectrometry with HPLC for the determination of taxol metabolites. Results of these LC/MS experiments indicate the presence of several previously not identified metabolites in both rat and human liver microsomal extracts.

43Q CAN ESTRONE AND TAMOXIFEN ACT AS MITOGENS FOR THE GROWTH OF ENDOMETRIAL AND BREAST CANCERS?

AW Pike. KK Leslie, PV Fennessey. Department of Pediatrics, Department of Obstetrics and Gynecology, University of Colorado School of Medicine, 4200 E. 9th Ave., Denver, CO, 80262. (303)270-7287.

Estrogens stimulate the growth of normal and malignant endometrial and breast epithelial cells by increasing the expression of growth factors. High levels of estrogens have been associated with an increased risk for developing breast and endometrial cancers. Estrogens control the expression of genes by binding to an intranuclear protein, the estrogen receptor, which can bind to DNA to regulate gene transcription and hence stimulate cell growth. Estradiol has the strongest affinity for the estrogen receptor. Estrone can be converted to Estradiol by 17|3-hydroxylase. Estrone is a "weaker" estrogen with significantly less affinity for the estrogen receptor; however, estrone is the primary estrogen present in postmenopausal women who are at greatest risk for developing breast and endometrial cancers. The research goal, using GCMS is to determine the percent conversion of estrone to estradiol in the endometrial and breast cancer cell lines, in the presence or absence of tamoxifen. The hormones will be extracted from media and cells with solvent, derivatised and subjected to analysis using GCMS. Results from these studies will be presented. This will help answer the clinically relevant question of whether it is estrone or estradiol that is responsible for the activation of gene transcription observed in these cells.

349 PHARMACEUTICAL METHOD VALIDATION - HOW MUCH AND WHY

Thomas Lay1 off, Food & Drug Administration, Division of Drug Analysis
1114 Market Street, St. Louis, MO 63101

The Division of Drug Analysis is one of the FDA laboratories which participates in validation of methods of analysis submitted by pharmaceutical firms as a part of the drug approval process. Our analysts frequently have difficulty reproducing these submitted methods.

It appears that many of the methods submitted for validation are developed with minimal regard to among-laboratory variance. Examples of problems encountered with methods submitted to the Division for validation during FY 92 and FY 93 and suggestions for improvements in submissions will be discussed.

350 DETERMINATION OF DI-(2-ETHYLHEXYL)PH0SPH0RIC ACID (HDEHP) IN HANFORD NUCLEAR PROCESS WASTE BY DERIVATIZATION GC/MS. Scott M. Donaldson, Jon E. Christensen, and Roll and R. Grabbe, Westinghouse Hanford Company, P.O. Box 1970, Richland, Washington 99352.

Di-(2-ethylhexyl)phosphoric acid (HDEHP) is an alkylated phosphoric acid used as a complexant in nuclear material processing. After prolonged exposure to the elevated pH's, temperatures, and radiation fields of these process streams HDEHP can degrade to extremely flammable components. These flammability concerns made it necessary to develop a method for the analysis of HDEHP. HDEHP is a very polar, high boiling compound and does not lend itself readily to direct gas chromatographic analysis, due to its decomposition at high temperatures. It was necessary to render HDEHP more volatile and less polar through derivatization. Only then could it be analyzed by gas chromatography/mass spectroscopy (GC/MS). The results of this work will be presented as well as the analysis of the flammable degradation products of HDEHP.

351 DETERMINATION OF URANIUM AND THORIUM IN TITANIUM BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Sho.ji Kozuka, Masaru Hayashi and Hideki Matsunaga, Research and Development Center, Toshiba Corporation, 1, Komukai toshiba, Saiwai, Kawasaki 210, JAPAN

Titanium is used as sputtering target material in dynamic random access memories. It is important to measure the impurity contents of titanium. In particular, uranium and thorium eject «~particles and cause the problem of soft errors. The purpose of the present investigation is to establish a sensitive and accurate determination method for detecting uranium and thorium in titanium by inductively coupled plasma mass spectrometry (ICP-MS). The sample was decomposed with hydrochloric acid in a PTFE pressure vessel, and subsequently added to hydrogen peroxide solution. Uranium was separated from titanium by anion exchange and thorium was separated from titanium by cation exchange. Adsorbed uranium and thorium were eluted by hydrochloric acid and sulfuric acid, respectively. Both effluents were almost evaporated to a dry state. The residual was dissolved by nitric acid. Finally the solution was measured by ICP-MS. When ICP-MS measurement was carried out, signal ion counts were suppressed by titanium matrix. Therefor, it was necessary to reject the titanium matrix. For this experiment, ion exchange separation was selected. The detection limits were 0.05 ppb.

LASER-EXCITED ATOMIC FLUORESCENCE SPECTROMETRY APPLIED TO REAL SAMPLE ANALYSIS - PRESENT STATE OF THE ART AND FUTURE POTENTIAL. ***Ven Cheam, Josef F. Lechner. Roland Desrosiers and Ivan Sekerka, Environment Canada, National Water Research Institute, P.O.Box 5050, Burlington, Ontario, Canada L7R 4A6***

There are already a large number of analytical procedures for trace metal analysis in routine use. The more common ones are based on Graphite Furnace - Atomic Absorption Spectrometry (GF-AAS), Polarography, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and more recently Mass Spectrometry (ICP-MS). Why then is there a need for another method ? Is it because in some cases these instruments and procedures are not sensitive enough for analysis of very low level samples without relying on tedious sample pre-treatment, which is time consuming and prone to introduction of and accumulation of contamination ? Laser-Excited Atomic Fluorescence Spectrometry (LEAFS) on the other hand has attracted much attention due to its ultra-sensitivity and great potential for use in service laboratories.

This presentation concentrates on three main areas - a brief description of LEAFS, its practical applications for analysis and a comprehensive literature review dealing with LEAFS application to the analysis of real samples. The results of LEAFS applications in this laboratory will be presented. It includes direct analysis of various aqueous matrices, comprising of Great Lakes waters, oceanic waters and Canadian Arctic snow and ice. The potential for routine use and speculations as to why Leafs has only been sporadically used in spite of its outstanding performance, will be elaborated.

PHOTOOXIDATION REACTIONS BASED ON SINGLET OXYGEN PHOTOCHEMISTRY. Emily Hergenreter Chris Jenson, Robert Milofsky, Department of Chemistry, Fort Lewis College, Durang CO 81301

Our laboratory is interested in the development and application of new detection techniques, particularly those involving photochemical reactions. The presence of singlet oxygen (**O2)** as an intermediate defines the mechanism of photooxidation termed type II photooxidation. Detection limits (l.o.d.'s) can be improved by 1-2 orders of^magnitude over UV absorption using photochemical amplification reactions based on **O2** photochemistry. Details on a new system which increases the yield of quinoline sensitized 0~ photooxidation of dimethyl furan by 25% will be presented Application of this technique to enhanced sensitivity in capillary electrophoresis will also be discussed.

ANGLE-RESOLVED PHOTOACOUSTIC SPECTROSCOPY FOR THE STUDY OF MOLECULAR ORIENTATION AT DIELECTRIC SURFACES. **Susan K. Doughty. Kathy L. Rowlen, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309**

Angle-resolved photoacoustic spectroscopy (ARPAS) is being developed as a technique to study molecular orientation at both metal and dielectric surfaces. ARPAS is based upon the photoacoustic signal generated as the angle between molecular transition dipoles and incident plane polarized light is varied. ARPAS offers the following advantages: the broad applicability of an absorbance technique, sensitivity similar to fluorescence, and applicability to both dielectric and metal surfaces. Initial efforts have focused on instrument design and signal characterization. Angle-resolved signals from two test systems exhibit the trend predicted by a simple two-dimensional model.

354 CHARACTERIZATION OF NUCLEOPHILIC ADDITION PRODUCTS OF THIOUREA ANn ACETYLHISTIDINE TO N-B-ALANYLDOPAMINE AND N-ACETYLDOPAMINE QUINn BY NMR SPECTROSCOPY. **Rongria Xni, Xin Huangi, Thomas D. Morgan?J Prakash2, Delbert D. MuellerZ, Karl J. Kramer2,3 ajM. Daie Hawley', i' + of Chem. and 2Biochem., Kansas State University, Manhattan, KS 665fj'6; 3rf Grain Marketing Research Laboratory, USDA, Manhattan, KS 66502.**

N-B-Alanyldopamine (NBAD) and N-acetyldopamine (NADA) are t important precursors for insect cuticle sclerotization, which is a compi process involving the oxidation of NBAD and NADA and adduct formation with structural proteins. Thiourea (TU) and N-acetylhistidine (NAcH) were us as model protein nucleophiles to react with NBAD and NADA quinones produc rt by electrochemical oxidation. The nucleophilic addition product (adducts) were purified by reversed-phase high performance liquid chromatography. *H and "C 1D-NMR and COSY, TOCSY and HMQC 2D-NMR method were performed to characterize the connectivity of TU and NAcH to NBAD and NADA. The results showed that both NBAD and NADA were attacked by the nucleophiles at carbon atoms in the aromatic ring. Under these conditions no addition product that was modified on the side chain aliphatic carbon atoms was found.

355 ALDEHYDE-FTJNCTIONALIZED SILANES AS A NEW IMMOBILIZATION REAGENT

Claudia Bruning and Joseph Grobe, Anorganisch-Chemisches Institut, Westfalische Wilhelms-Universitat, Wilhelm-Klemm-Str. 8, 48149 Munster, Germany

The immobilization of biological components is an important step in many different fields of research. For example, in bioanalytical chemistry and for the construction of biosensors the fixation of biomolecules is necessary. In many cases, silicon organic compounds are used as connecting links between surface and biological compound. We synthesized aldehyde-functionalized silanes as a new class of spacer molecules for silica surfaces. The aldehyde group can be used to attach biomolecules directly to the surface using free amino functions for the reaction forming a Schiff s base. In contrast to the most popular immobilization technique using 3-aminopropyltriethoxysilane (APTES), no bifunctional crosslinker is required. Therefore, the new one-step immobilization method is especially fast, reproducible, and convenient. The results of the immobilization of glucose oxidase on controlled pore glass (CPG) with different techniques and reagents were compared using a photometrical activity test of the enzyme. The best results concerning reproducibility, activity, and long-term stability of the immobilization were obtained with the aldehyde-functionalized silanes. We will additionally present first results on immobilization of antibodies using this new method.

356 GENERAL METHOD FOR THE DETERMINATION OF EVAPORATION RATES FOR MULTICOMPONENT SOLVENTS CONTAINING HALOGENATED COMPOUNDS.

Jimmy L. Seidel and Linda S. Johnson, U.S. Environmental Protection Agency, National Enforcement Investigation Center, Building 53 Box 25227, Denver Federal Center, Denver, Colorado 80225.

In order to determine if illegal disposal of halogenated solvents had occurred ("F" listed wastes 40 CFR § 261 Appendix VII) we found it necessary to evaluate claims of solvent loss through evaporation. The solvent of interest was a hydrocarbon based electrical circuit cleaning solvent containing dichloromethane and tetrachloroethene. Because of the complexity of the mixture, theoretical predictions of solvent loss seemed inappropriate; therefore, a two-fold experimental strategy was devised. Scale models of cleaning equipment were fabricated and the loss of bulk solvent monitored gravimetrically under various conditions. During the gravimetric determinations of bulk solvent loss, aliquots were removed to determine the concentration of halogenated compounds. The nature of the matrix made most common GC methods impractical for determining the concentration of halogenated compounds and necessitated the use of a coulometric total organic halogen analysis. A detailed summary of the experimental strategy, results, and problems encountered will be presented.

357 **CHEMICAL AND BtOLQGICALC EFFECTS *Of* GOLD MINE TAILINGS ON LARDER LAKE ONTARIO.** ***Fernando* Rosa. Alena Mudroch, and Trefor B. Reynoldson, Aquatic Ecosystem Restoration Branch, National Water Research Institute, Environment Canada, 867 Lakeshore Rd., Burlington Ontario, Canada, L7R 4A6.**

Mining activities, for the recovery of base metals and precious metals, generate a considerable amount of tailings and waste rock. The tailings are usually disposed into tailing ponds. Liquid wasters are discharged into surface water systems. An investigation was carried out to evaluate effects of effluent discharge from a gold mine on the ecosystem of Larder Lake in Northern Ontario.

Bottom sediments and surface and bottom water samples were collected at thirty-eight sampling stations in Larder Lake. Concentration profiles of nutrients, chlorophyll, temperature, conductivity, and pH were obtained in the water column at selected sampling station. Pore water from the bottom sediments was collected in Larder Lake. Two lakes, located in the same watershed, were selected as control or references sites for the study.

The concentrations of Ni. Cu and As *in* the lake water are 29, 33 and 39 times above Environment Canada Guidelines, for Ni, Cu and As, respectively. The results of the investigation indicated that primary production and the benthic community in Larder Lake are severely impaired, most likely due to widespread water and sediment toxicity.

358 **COLORJMETRIC DETERMINATION OF SELENIUM AS SELENTTE OR SELENATE IN MINERAL PREMLXES.** **Jeffrey A. Hurlbut. Roger G. Burkepile, Philip J. Kijak, and Carolyn A. Geisler, Food and Drug Administration, Denver Veterinary Analytical Section, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087**

Selenium is both a toxic and an essential trace element for animals; Se is frequently added to feed using mineral premixes; and these premixes contain Se as either selenite or selenate as well as a large amount of inorganic salts such as calcium carbonate. We devised a colorimetric procedure to analyze the Se in these mineral premixes. The method involves a nitric acid digestion, filtration, treatment with HC1 and EDTA, derivatization with 3,3'-diarmnobenzidine, extraction into toluene, and measurement of the absorbance at 420 nm. Typical Se recoveries for calcium carbonate based premixes containing iron salts and Se as either selenate or selenite range from 90 to 100% with coefficients of variation between one and five percent. Results of numerous analyses as well as results from a four lab inter-laboratory study are presented.

359 **DETERMINATION OF NEOMYCIN IN ANIMAL FEED AT THERAPEUTIC AND RESIDUE LEVELS BY CAPILLARY GAS CHROMATOGRAPHY.** **Susan B. Clark. Robert J. Schmid, W. Douglas Rowe, Jeffrey A. Hurlbut, and Carolyn A. Geisler, US Food and Drug Administration, Denver Veterinary Analytical Section, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087.**

A rapid and sensitive gas chromatographic method for the determination of residue and therapeutic levels of neomycin in animal feed is described. Sample preparation includes acid extraction, ion-exchange clean-up of extract, a two-stage derivatization, and toluene extraction with a water wash. Recoveries, CV's, detection limits, and experimental conditions are presented.

360 **DETERMINATION OF HERBICIDE RESIDUES: SIMAZINE, ATRAZINE, AND PROPAZINE IN CATFISH BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY.** **DavjdXjIcJJajigl Robert K. Munns, Jose E. Roybal, Jeffrey A. Hurlbut, and Austin R. Long Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087.**

A liquid chromatographic method is described for the simultaneous determination of triazine herbicides, simazine (SIM), atrazine (ATZ), and propazine (PRO) in catfish in the 12.5 -100 ppb range. The herbicides are extracted from catfish with ethyl acetate, followed by solvent partitioning between acetonitrile and petroleum ether, with additional cleanup on a C_{1g} cartridge. A Supelcosil LC-18-DB column is used for LC separation with UV determination at 220 nm. The isocratic mobile phase is a mixture of methanol and water. Mean recoveries from catfish were 88.7% for SIM, with a standard deviation (SD) of 6.84 and a coefficient of variation (CV) of 7.72%. Mean recoveries for ATZ were 96.9%, with a SD of 7.79 and a CV of 8.04%. Mean recoveries for PRO were 91.7% with a SD of 6.26 and a CV of 6.82%

DETERMINATION OF FLUMEQUINE, NALIDIXIC, OXOLINIC AND PIROMIDIC ACID RESIDUES IN CATFISH BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-FLUORESCENCE/UV DETECTOR. Robert K. Munns, Sherri B.. Turnipseed, Allen P. Pfenning, Steven M. Plctkas', Jose E. Roybal, David C. Holland and Austin R. Long Animal Drugs Research Center, P.O. Box 25087, Denver District, Food and Drug Administration, Denver Federal Center, Denver,' CO 80225-0087

" Division of Seafood Research, Food and Drug Administration, P.O.Box 158, Dauphin Island, AL 36528

A liquid chromatographic method for determining flumequine, nalidixic, oxolinic and piromidic acid residues in catfish muscle is presented. Also described is a gas chromatographic\mass spectrometry confirmation of these residues. The extraction and cleanup procedures are the same for both determination and identification. Sample work-up involves homogenizing the tissue with acetone, defatting with hexane and extracting these compounds into chloroform. The sample is further purified by first partitioning into base and subsequently back extracting into chloroform after acidifying the aqueous phase. After solvent is evaporated, the residue is diluted with mobile phase and the analytes are determined by HPLC using fluorescence detection at 325 nm excitation and 365 nm emission. Separations were made on a 5um, PLRP-S polymer column using an isocratic buffered-acetonitrile-tetrahydrofuran mobile phase. Each quinolone was used to foritfy catfish muscle at levels of 5, 10, 20, 40 and 80 ppb.

362 DETERMINATION OF MALACHITE GREEN AND METABOLITE, LEUCOMALACHITE GREEN IN CATFISH (ICTALURUS PUNOTATUS) TISSUE BY HIGH PRESSURE LIQUID CHROMATOGRAPHY WITH VISIBLE DETECTION (LC/VIS). JOSE E. ROYBAL, ALLEN P. PFENNING, ROBERT K. MUNNS, DAVID C. HOLLAND, JEFFREY A. HURLBUT AND AUSTIN R. LONG. Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087

A method is presented for the determination of malachite green (MG) and metabolite, leucomalachite green (LMG), residues in catfish tissue. The analytes are extracted from tissue with acetonitrile/buffer and partitioned into methylene chloride. Final cleanup and isolation is performed on neutral alumina SPE and propylsulfonic acid cation exchange SPE columns prior to LC analysis. Liquid chromatography, using visible detection (LC/VIS) analysis coupled with PbO_2 post column oxidation, is performed by isocratic elution with a buffered mobile phase from a cyano colurhn. Recoveries of MG ana LMG from fortified catfish tissue were 72.9%, 1.92%RSD (23 ppb.), 75.5%, 6.85%RSD (11 ppb), 69.6%, 6.93%RSD (5.7 ppb) and 87.4%, 2.92%RSD (21 ppb), 88.1%, 5.94%RSD (10 ppb), 82.6%, 11.5%RSD (5.3 ppb), respectively. The method was applied to MG-incurred catfish at depuration times of 0, 2, 4, 8 and 24 hours. The average levels of residual MG and LMG in the 24 hour depuration catfish, tissue was 73.4 ppb and 289 ppb. respectively.

363 **DETERMINATION OF FLUNIXIN IN MILK USING LIQUID CHROMATOGRAPHY A11H MS-SIM CONFIRMATION.** *Heidi S. Rupp, David C. Holland, Robert K. Munns, Sherri B. Turnipseed, and Austin R. Long.* Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Building 20, P.O. Box 25087, Denver, CO 80225-0087.

A liquid chromatographic (LC) method was developed for the determination of flunixin (FNX) in raw bovine milk. The milk was acidified, mixed with silica gel and the mixture was packed into a chromatographic column. The column was defatted with water-saturated DCM-hexane (30:70, v/v), and the analyte eluted with EtOAc. The EtOAc was shaken with water at pH 3.5, the water discarded, and the EtOAc then shaken with 0.1 M NaOH. The water layer was drained and passed through a primed C18 SPE column, and eluted with EtOAc. The EtOAc was dried under N_2, taken up in a 50/50 solution of MeOH/(5mM TBA-H_2P0_4 + 2mM NaOH), sonicated and filtered. FNX was determined by HPLC using a C18 column (ODS Hypersil), a mobile phase of A:MeOH and B-5mMTBA-H_2P0_4 + 2mM NaOH (A:58%, B:42%), and a diode-array ultraviolet detector at 285 nm. FNX was determined in raw milk at five spiking levels (5,10, 20, 40 and 80 ng drug/mL milk). Absolute recoveries ranged from 69.6% to 74.4%, and relative standard deviations ranged from 1.1% to 6.9%. The limit of determination was 5 ng drug/mL milk. A lactating cow was dosed *iv* (2.2 mg/kg) with flunixin meglumine (Banamine) to generate incurred milk residues. FNX residues ranged from a high of 7.34 ng/mL at 16 hrs post dose, to 1.74 ng/mL at 24 hrs post dose, both with additional li-glucuronidase treatment. The presence of FNX in incurred milk was confirmed using GC/MS-SIM (EI) at ions 310, 295, 277, 263, 251, and 249 m/z.

365 **A ROUTINE ANALYTICAL METHOD FOR THE MONITORIZATION OF NAPHTHALENE DEGRADATION BY HRGC AND HPLC.** Eduardo P. Mateus and Rui B. Ganho. Department of Environmental Sciences and Engineering, New University of Lisbon, Quinta da Torre, 2825 Monte de Caparica, Portugal.

A routine analytical method is described for monitorization of naphthalene degradation in a lab scale composting process. An exhaustive steam distillation/solvent extraction procedure (SDE), using the Veith and Kiwus apparatus, was employed to extract the analyte and screen the substract. Quantitative determinations were performed by High Resolution Gas Chromatography (HRGC) with a DB-5 (J&W), 30 m x 0.32 mm LD. capillary column and a flame ionization detector (FID). In order to achieve better sensivity, quantitative determinations were also performed by normal-phase high-performance liquid chromatography (HPLC) using a Fluorescence detector. Good agreement was obtained between GC and HPLC quantitative determinations. Recoveries were higher than 80% and the variation coefficient was less than 10 %. In the proposed procedure, the samples were blended with water and refluxed for 1-2 h, using a maximum of 10 ml hexane as the extraction solvent, through which the distillate percolated and the chemicals partioned. This method is cheaper, less labour intensive and less time-consuming than traditional extraction methods. It uses small amounts of solvent and the final extract is colorless and suitable for direct GC analysis, avoiding further concentration and clean up steps.

366 **DETERMINATION OF SELENIUM IN NATURAL WATER BY GF-AAS AFTER SOLVENT EXTRACTION PRECONCENTRATION.** Lan-Xiang Meng, V.Nanto, Mari Walls, Uno Wegelius, A.L. Makela, P.Laihonen, w.Wang and Zhi-Min Li, University of Turku, 6-14-6 Dong Da Qiao Lu, Chaoyang District, Beijing 100020, China.

The total amount of selenium in finnish natural water is usually < 250 ng/1. Different species of selenium, both inorganic and organic, may be present at few ng/1 so can not be measured directly with the instrumental techniques normally available. As a quite sensitive, the method is based on use of diethyldithiocarbamate (DEDC) to co-"Plex the trace selenium from the natural waters, with subsequent separation of the complex by solvent extraction and guantification by GF-AAS. The concentration coefficient is 10 . The limit of detection is 0.01 ppb for a 250 mi sample. The precision (KSD) at the 10 ng level is better than 5 %. The recovery is 96.6 % (93.5 - 99.6 %). Accuracy of results was assessed by independent, analytical techniques (ICP-MS). The comparison between GF-AAS and ICP-MS results of analysis of natural water samples indicates good agreement.

367 **DINOPHYSISTOXIN-2 : A NEW SHELLFISH TOXIN IN EUROPE.** Eoin P. Carmody, Kevin J- Jqmos and Sean S. Kelly, Chemistry Department, Cork RTC, Bishopstown, Cork, Ireland.

An okadaic acid (OA) etiology has been demonstrated for most outbreaks of diarrhetic shellfish poisoning (DSP) in Europe An isomer of OA, named dinophysistoxin-2 (DTX2), has recently been found in Irish waters and in 1991 was the major toxin during a prolonged infestation (4 months) in cultivated mussels along the south west coast of Ireland. DSP toxins are associated with red tides of *Dinophysis* sp. A recent Spanish study also confirmed the presence in these flagellates of both OA and DTX2 using fluorimetric HPLC following derivatisation with anthryldiazomethane. Two commercially-available ELISA methods, designed to determine OA were examined for potential use in the analysis of samples containing both OA and DTX2. One of these ELISA methods showed good cross-reactivity with DTX2. Comparison of results obtained by this method with those of a validated HPLC protocol was satisfactory. Rapid DSP-screening of shellfish in Ireland and other European countries may thus be possible using ELISA.

3 6 8 **ASSESSMENT OF CHEMICAL PLANT AIR EMISSIONS ON AN URBAN ENVIRONMENT.** Kevin J.James, Mary A. Stack. Cork RTC, Bishopstown, Cork, Ireland.

This six month study was initiated to assess the effect of organic solvents from a cluster of industries on ambient air quality. A local population of 800 people who live within a 500 meter radius adjacent to chemical industry were identified as potentially at risk. The study was based in Little Island Industrial Estate, located three miles east from Cork, the second largest city in the Republic of Ireland with a population of 130,000. Eight chemical sector companies operate in this area and they constitute the largest block of chemical manufacturing in Ireland. Six of these companies are licensed to discharge organic solvents under permit. The total mass loading in kilograms/hour was determined for each company and the individual solvents identified using gas chromatography coupled to photoionisation and mass selective detectors. A meteorological station was situated within the study zone to measure local conditions, particularly wind speed and direction. Ambient air downwind from the chemical companies was monitored for specific solvents based on emission inventories. This study showed that, although there was evidence of organic solvents in the ambient environment, the impact on overall air quality was not significant to pose a threat to public health.

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DETERMINATION OF HALOGENS IN A PETROLEUM PRODUCT BY ION CHROMATOGRAPHY

H. L. Tucker

A rapid, high-performance ion chromatography (HPIC) method with isocratic separation and the anion self-regenerating suppressor (in the chemical suppression mode) (specifically for the determination of fluoride, chloride, bromide, and iodide in a petroleum product) is discussed. This is a proposed new method for a production laboratory within Martin Marietta's Y-12 Plant Analytical Services Organization.

Currently, there is no method within the production laboratory for total halogens, nor does available literature or Dionex suggested HPIC methods show fluoride, chloride, bromide, and iodide in a single run. This prompted an experimental preparation method to be developed with subsequent analysis by HPIC. A precision and bias study was done to document the effectiveness of the new method.

427 **IDENTIFICATION OF GENTAMICIN BY GAS CHROMATOGRAPHY/ NEGATIVE ION CHEMICAL IONIZATION MASS SPECTROMETRY (GC/NICIMS).** **Barbara S. Portz, Food and Drug Administration, Denver Federal Center, Bldg 20, Denver, CO 80225 and Thomas M. Heinze, National Center for Toxicological Research, Jefferson, AR 72079**

Gentamicin, a widely used primary aminoglycoside antibiotic, is used to treat Gram negative infections in animals. (, the concern that the antibiotics may remain in the tissue and milk, an analytical method was previously developed • the laboratory for detection of gentamicin and neomycin residues by GC with electron-capture detection. An identification oethod by GC/MS would be useful for confirmation of gentamicin. Since there are four major components of gentamicin (C Cj Ci, and C2J each with slightly different chemical structures comprising 10-35% of the total, the problem was extremely complex. The molecular weights of these four components after derivatization with trimethylsilylimidazolefTMSI) ind heptafluorobutrylimidazole (HFBI) are between 1600 and 1700 amu. The molecular ions were targeted as well as the ions produced due to the hydrolysis of one of the rings (garosamine) and those possibly due to TMS or heptafluoro losses or incomplete derivatization. SIM analysis of these ions increased the sensitivity. The HP 5989A MS (Engine) with an extended mass range of 2000 amu and a high energy dynode was used and negative ion, chemical ionization with methane proved to be the best technique. It was found that the gentamicin standard would derivatize well only in the presence of an aliquot of extract produced by taking a control (tissue or milk known to be free of gentamicin) through the cleanup procedure. To simplify this and make the method more widely accepted, replacement of the protein moiety was explored.

369 **A NEW MICROWAVE INSTRUMENT FOR RAPID SOLVENT EXTRACTIONS.** **Todd Kierstead. Robert Revesz, CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200**

Liquid-solid extractions are among the oldest and most widely practiced sample preparation techniques for chemical analysis. They are performed on such diverse materials as plastics to determine additives, raw or processed foods to determine residual pesticides, and soils, sediments and tissue to measure the environmental impact of a variety of organic compounds. Frequently, the most time consuming steps in chemical analysis are these sample preparations. Microwave heating of organic solvents in closed containers can significantly reduce the extraction time required for the determination of many complex analytes. This paper presents data on priority pollutants in sediment and soils using traditional solvents with microwave extraction techniques. In addition, we have followed a more fundamental approach to improving extractability by selecting solvents with good dielectric properties. These approaches permit sample extraction times to be reduced from hours to less than 30 minutes. Studies have been conducted in microwave equipment specifically designed for safe operation using organic solvent extraction. The microwave heating system includes a specially designed solvent evacuation system to prevent solvent vapors from reaching their lower flammability limits. The system also includes a solvent vapor detection device and air flow switch designed to turn off the microwave power if vent vapors are detected or no air flow is detected inside the microwave heating cavity. To control extraction conditions a unique microwave transparent temperature sensing system is used to control the extraction emperarure to within ±2° Celsius. These systems will be described and their advantages discussed.

370 **GOOD LABORATORY PRACTICES (GLPs) IN THE NON-REGULATED LABORATORY.** **Mark J. Lehr. U.S. Environmental Protection Agency, National Enforcement Investigations Center, Bldg. 53 Denver Federal Center PO Box 25227 Denver, Colorado 80225.**

To one degree or another, scientists have always worked within a set of principles which they consider to be good laboratory practices. On October 16, 1989 chemical testing laboratories took particular notice when EPA extended the realm of Good Laboratory Practice (GLP) Standard regulations 40 CFR sections 160 and 792. These new regulations, which govern testing for pesticides registration and toxic chemical manufacturing, helped the scientific community to standardize the concept of good laboratory practices. However, there still exists a large number of testing laboratories which are not required to conduct analysis under the GLP Standard regulations, but which still want to (or should) operate under principles of good laboratory practice. The question arises; how does one utilize the GLP regulations to establish confidence in the quality of data produced by these laboratories?
While GLPs serve as valuable guidelines, not all of the requirements are directly applicable to unregulated non-GLP analytical laboratories. Unregulated laboratories could selectively create a good laboratory program (glp) tailored to meet their own applications essentially meeting the "spirit" of the GLP regulations. Such programs could be developed in a Quality Assurance Project Plan (QAPP) or equivalent which could be used to guide the unregulated laboratory. My talk will address the basic fundamentals of the GLP regulations and how they can be applied to good laboratory practices in a non-regulated laboratory.

'1 **PARTNERING AS A TOOL FOR IMPROVING ANALYTICAL LABORATORY PERTORMANCE.** **Moheb M. Khalil and Terrence P. Killeen, Westinghouse Savannah River Company, Aiken, SC 29808 and George C. Greene, III, and James T. Chambers, General Engineering Laboratories, Charleston, SC 29417.**

Westinghouse Savannah River Company (WSRC) contracted several laboratories in 199S to conduct 175,000 organic, Inorganic, and radiological analyses on samples collected from 1,500 monitoring wells. WSRC's responsibility is to ensure that each laboratory provides reliable and comparable analytical results. A WSRC team developed a Quality Assessment Program (QAP) for monitoring the performance of subcontracted laboratories. The program uses three types of evaluations. The first type is an evaluation of quality control samples sent quarterly to each lab. The second type is a Mean Relative Difference fMRD) statistics that identifies intralaboratory differences of replicates vs. blinds and interlaboratory differences of split samples. The third type is an on-site performance evaluation of laboratory facilities and operations. The presentation will address one example of a success story of the use of MED statistics to identify quality problems and to measure the effectiveness of corrective action through a partnering relationship developed with General Engineering Laboratories, This effort resulted in reducing the level of methylene chloride contamination in the volatile organic laboratory from just under 10 ppb to teas than 0.5 ppb during a Uiree-year period. It will be demonstrated that high-quality analytical services can be obtained cost-effectively through a strong partnership.

3'[2] **QAING THE QUALITY ASSURANCE UNIT.** **William N. Palmer. U.S.EPA, NEIC, P.O. Box 25227, Denver, CO 80225.**

In the conduct of Federal Insecticide Fungicide and Rodenticide Act (FIFRA) Good Laboratory Practice Standards(GLP) inspections of testing laboratories the EPA, in essence, conducts a quality assurance inspection of the Quality Assurance Unit (QAU) of the laboratory. Pesticides used in the United States must be registered. To be registered the pesticide must meet FIFRA regulations. To meet these regulations the scientific tests which support the registration application must be conducted under GLP regulations. At least one phase of each of these tests must receive a quality assurance inspection. The QAU should be involved in the approval of the protocol for conduct of the scientific tests before the tests are done. The QAU should also observe at least one phase of the experiment to assure that the tests are conducted according to the protocol. When an EPA inspector conducts a GLP inspection of the testing laboratory or field site the inspector compares the raw data produced during the test with the report submitted to EPA. When an EPA inspector finds GLP problems at a facility, this usually indicates that the QAU has not adequately fulfilled their responsibilities and has not recognized problems during the course of the study.

373 **REMOTE ATMOSPHERIC GAMMA-RAY SPECTROSCOPY WITH HPGe DETECTORS and SATELLITE DATA TRANSMISSION.** **Colin G. Sanderson, Norman Latner, and Richard Larsen, Environmental Measurements Laboratory, U.S. Department of Energy, 375 Hudson Street, New York, New York 14414-3621.**

Since 1963 the Environmental Measurements Laboratory (EML) has maintained a worldwide network of surface air sampling stations. At these stations, airborne particles are collected on highly efficient polypropylene filters from about 8,000 m^3 of air each week. The filters are then sent to EML where they are analyzed for gamma-ray emitting radionuclides. In order to obtain almost real time gamma-ray analyses from remote sites, third generation remote atmospheric measurement systems (RAMS) were developed by EML. These systems include a lead shielded mechanically-cooled 35% (rel.) HPGe n-type detector, a programmable multichannel analyzer, a programmable transmitter, gel cell power supply, and a portable computer. The computer controls the entire system data flow, and parameters. These RAMS use geostationary satellites that can receive 649 bytes of data each hour and a complete 1800 channel spectrum in 7 h.

In December of 1993 a HPGe RAMS was installed at Geyokcha, Turkmenistan. Because of unreliable AC power at this site a UPS was also installed. The unusual power requirements of the mechanically-cooled germanium detector required significant modifications to both the control software and the UPS.

374 POSSIBILITIES AND LIMITATIONS OF THE USE OF NATURALLY-OCCURRING SULPHUR-35 IN SMALL WATERSHEDS. **Robert L. Michel, U.S. Geological Survey, 43! National Center, Reston, VA 22092, John T. Turk, U.S. Geological Survey, MS 415,' Box 25046, Bldg. 53, Denver Federal Center, Denver, CO 80225, David L. Naftz, U.S. Geological Survey, 1745 West 1700 South, Salt Lake City, UT 84104.**

Suiphur-35 is a naturally-occurring radioisotope of sulphur with a half-life of 87 days. It is produced by cosmic-ray spallation of atmospheric argon, and is then deposited on the earth's surface by wet or dry deposition. The short half-life of sulphur-35 makes it an ideal tracer for studying hydrologic processes that occur on the timescale of one year or less. The U.S. Geological Survey Tritium Laboratory has been studying the distribution of sulphur-35 at selected watersheds for the last two years. Present limitations of its use due to technical and hydrologic problems will be examined, and watersheds where it can used as a tracer will be discussed. Sulphur-35 results will be presented from two watersheds: 1. The Ned Wilson Lake watershed near Meeker, Colorado. 2. The glacier fields in the Wind River Range in Wyoming.

STATISTICAL PROCESS CONTROL FOR ALPHA SPECTROSCOPY. **William M. Richardson, Richard S. Seymour, Ronald E. Majoras, OXFORD Instruments Inc., 601 Oak Ridge Tpk, Oak Ridge, TN 37830, and Irene Joo, ACCU-LABS Research, 4663 Table Mountain Dr., Golden, CO 80403.**

Statistical process control allows for the identification of problems in the radioanalytical alpha spectroscopy process before they occur, unlike standard laboratory QC which only identifies when a process has failed. Many statistical process control tools are directly applicable to alpha spectroscopy. These tools allow analysis of process bias, precision, accuracy and reproducibility as well as process capability. Parameters affecting the instrument performance are often monitored, tracked, and analyzed using QC or statistical process control methods. Examples include background, vacuum level, temperature, equipment supply voltages, amplifier and preamplifier output, amplifier gain, detector leakage current, bias voltage, electronic puller FWHM, puller position and detector efficiency. Furthermore, these instrument parameters can effect relationships that can improve the accuracy of the overall measurement process. To accomplish these benefits, other parameters affecting the measurement must also be tracked. Peak FWHM, peak centrold, chemical recovery, control sample results, sample duplicates and sample blanks all play an important role in determining if your process is in control. Many laboratories plot only the mean value of an important parameter which does not provide enough information to determine if a process is in control (standard laboratory QC). Statistical process control groups data into subgroups to obtain an average of the subgroup and a measure of its dispersion. By standardizing each observation or set of observations, it is possible to plot short runs of data and still examine long-term control which can cause unnecessary down time in the laboratory at a critical time. Examples are provided of how SPC can be used as a tool to predict when the process is going to fail. This allows for an orderly and timely shutdown of the process for preventative maintenance and avoids costly repeat analyses of samples.

376 **RADIOTRACER STUDY OF ELECTRODE SURFACES.** **Maria Gamboa-Aldeco. Krzvsztof Fxflnaszczuk. and Andrzej Wieckowski, Department of Chemistry, University of Illinois, 600 South Mathews Avenue, Urbana, Illinois 61801.**

Radiotracer methods are *in-situ* techniques that use a radioactive label to •tor molecules of interest adsorbed at the electrode/solution interface, "^ffotracer methods are label specific and are based on a straightforward relationship tween surface count rates and surface concentrations. Therefore, the determination *f* surface concentration is model independent and unambiguous. During the ntation we w1--n demonstrate a technique, that was developed for a ^racterization of adsorption at smooth electrode surfaces. We will show how well do the radiochemical data compare with results obtained by other techniques. We will how that radiotracer methods for adsorption measurements offer some unique ^vantages. Specifically, one can obtain the following data and experimental lationships: (i) surface concentrations of adsorbates. (ii) rates of adsorption, (iii) potential dependence of adsorption, (iv) concentration dependence of adsorption, (v) temperature dependence of adsorption, (vi) rate of surface diffusion of adsorbate, (vii) ionic strength effects on electrode adsorption. Using combined coulometric and radiotracer measurements one may deduct the identity of adsorbed species. Finally, one can also test for adsorption reversibility through measurements of exchange of labeled surface species with unlabeled solution species.

IMPROVEMENTS IN ALPHA SPECTROMETRY. **Wayne P. Graves.**
377 **ORDELA, Inc., 1009 Alvin Weinberg Drive, Oak Ridge, TN 37830, W. Jack McDowell, ETRAC, Inc., 1009 Alvin Weinberg Drive, Oak Ridge, TN 37830**

Improvements will be discussed that result in better resolution, virtual 100% counting efficiency, and faster turnaround times for alpha spectrometry. Specific applications will be discussed, including several sequential analysis protocols for radionuclides in waters that can yield sensitivities of < 1 pCi/L. Other samples, such as soils, oils, effluents, bioassay, and biological, are easily analyzed with no sample self-absorption limitations and no.possibility of sample cross-contamination. Use of a commercially available peak-fitting software package will be reviewed. Time comparisons will be made with other counting methods. Other pertinent topics may be addressed as time and audience interest permits. The entire system is inexpensive, small, light-weight, and ideally suited for mobile laboratories as weii as analytical labs. A NEW, self-contained, portable instrument is also available.

USING GEOLOGY TO PREDICT RADON OCCURRENCE: SCALE CONSIDERATIONS
R. Randall Schumann U.S. Geological Survey, MS939 Federal Center, Denver, CO 80225-0046

The selection of data types and levels of detail for assessments of geologic radon potential depends in large part on the size of the area being evaluated. Many of the complex interactions between geologic, pedologic, meteorologic, and building construction factors can be generalized or ignored in radon characterizations of a state- or county-sized area, but they must be understood and addressed in detail in order to adequately characterize areas on the order of a single homesite or neighborhood. Some theoretical models and equations that describe different aspects of radon generation and transport from a parent radium atom into the living space of a home have been developed, but because many of these factors are interrelated in a complex fashion, these models are incomplete or must make a number of limiting assumptions that prevent characterization of the site in sufficient detail. A representative list of typical assessment scales follows. As a general rule, it is necessary to understand processes and provide detail at two scales larger (farther down the list) than the scale of the area to be assessed.

SCALES OF RADON SITE EVALUATIONS

1. **State-sized areas (or larger)**
2. **County-sized areas** *(climate)*
3. **Sub-county** *(rock/soil units)*
4. **Individual building sites** *(house construction characteristics)*
5. **Macroscopic site properties** *(permeability, soil profiles, meteorotogic effects, con/advective gas transport)*
6. **Molecular-scale properties of radon and soil particles** *(radon emanation, chemical processes)*

THE NATURE AND TIMING OF URANIUM UPTAKE IN WETLANDS: SOME UNIQUE PERSPECTIVES BASED ON RADIOGRAPHY AND U DECAY-SERIES ISOTOPES.
Robert A. Zielinski. Charles A. Bush, and John N. Rosholt (deceased), U.S. Geological Survt Denver, Colorado 80225.

Radiographic and isotopic measurements that are unique to uranium-based studies provide some important insights regarding the nature and timing of U uptake in naturally uraniferous peats. Fission-track radiography of peat thin sections provides direct observation of the distribution of trace levels of U on a microscale. Peat can be monitored for changes in extent of U uptake as a function of depth or hurnification. Relative U concentrations can be estimated from the density of fission tracks. For late Pleistocene and Holocene age peats experiencing input of natural U for thousands of years, apparent U-emplacement ages are based on the in situ buildup of the radiogenic daughter product ^{230}Th (ti/2=75 ka) and an assumption of closed-system behavior at depth. The validity of these ages can be tested by depth-related sampling and reference to independent estimates of depositional age (dated ash layers, ^{14}C ages). The more probable open-system behavior of chemically dissimilar, shorter lived daughter products (such as ^{226}Ra) can be estimated by the degree of radioactive disequilibrium with their parent isotopes (in this case ^{230}Th). The ^ U / $^{2\ 3}$ ^ isotopic activity ratio may be useful for identifying peats with significant U inputs from unusual sources, such as acid mine drainage or phosphate fertilizer.

380 **PLUTONIUM-239+240 AND AMERICIUM-241 IN SOILS EAST OF ROCKY FLATS, COLORADO.**
M. Iggy Litaor, M.L. Thompson, G.R. Barth, and P.C. Molzer, EG&G Rocky Flats Plant, Building 080, Golden, CO 80402-0464, and Agronomy Department, Iowa State University, Ames, Iowa 50011-1010.

Soils east of the Rocky Flats Plant (RFP) near Golden, Colorado were contaminated with Pu-239+240 and Am-241 as a result of past waste-storage practices. The physicochemical parameters that govern the actinides distribution in the soil are poorly understood. Twenty-six soil pits at various distances and directions from a contaminated site at Rocky Flats were excavated, sampled, and analyzed for actinide activities as well as selected physical, chemical, and mineralogical attributes. Plutonium-239+240 and Am-241 activities in the soils ranged from 164,280 Bq/Kg to 0.0037 Bq/Kg, decreasing with distance from the source. More than 90 percent of the Pu-239+240 and Am-241 activities were confined to the upper 12 cm of the soil, regardless of the soil characteristics, or distance and direction from the source. Evidence of preferential transport in macropores formed along decayed root channels was observed in 4 soil pits and had translocated Pu-239+240 to a depth of 90 cm. This transport mechanism increased by a factor of 30 the level of Pu-239+240 activity at this depth. Earthworm activity is probably important in the redistribution of actinides in the upper 40 cm of many of the soils investigated. Planning of future remedial activities at Rocky Flats should consider the finding of this contaminant-transport study.

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Abstract Not Available

qo **A SOIL MONITORING SYSTEM FOR ASSESSING CONTAMINANT TRANSPORT: PLUTONIUM-239+240 AND AMERICrUM-241.** **M.Z. (Iggy) Litaor, G.R. Barth, P.C. Molzer, E.M. Zika, H. Daniels, and J. Moffitt, EG&G Rocky Flats Plant, Building 080, Golden, CO 80402-0464.**

Soils at Rocky Flats Plant (RFP) near Golden, Colorado have been contaminated with Pu-239+240 and Am-241 as a result of past waste-storage practices. It has been suggested, that once actinides were deposited on the soil surface at RFP they were largely immobile. However, recent findings indicated that Pu-239+240 and Am-241 may eventually leach through the soil system to groundwater. If actinide transport is indeed significant, it will have an enormous impact on the cost and schedule of remedial action. The fate and transport of actinides in soil as well as the soil physicochemical properties that govern the behavior of these actinides are poorly understood. A soil water monitoring system (SWMS) was installed to gather real time data on freely flowing soil interstitial waters, water content, matric potential, soil temperature, and precipitation. The SWMS also collects soil solutions at different matric potentials for actinide analyses. The movement of water and actinides was evaluated by studying natural and simulated rain, which ranged widely in intensity, frequency, and duration.

383 **CARBON-14 TRANSPORT AT YUCCA MOUNTAIN,** **Donald C. Thorstenson, U.S. Geological Survey, Box 25046, Lakewood, Colorado, 80225**

An open borehole, USW UZ-6S, at the crest of Yucca Mountain, Nevada, exhausts approximately 1.3×10^6 m^3 of gas annually. The 158 m borehole blows continuously during the winter due to thermal-topographic convection. The gas flow occurs in fractured volcanic tuffs of the Tiva Canyon welded hydrogeologic unit.that comprises the top 125 m of the mountain. Nitrogen, oxygen, and argon, are at atmospheric concentrations throughout the Yucca Mountain crest unsaturated zone, an important consideration for radionuclide transport. The CO_2 concentration of the gas is 0.12 volume %, with an average $\delta^{13}C$ value of -17‰. The average ^{14}C content of carbon dioxide in the gas is 108 percent modern ccarbon. The gas thus post-dates atmospheric nuclear testing. The gas appears to originate in soil zones within a few hundred meters of the borehole, and to be advectively transported through the shallow unsaturated zone and out the borehole. The shallow unsaturated zone is separated from the proposed repository horizon, the Topopah Spring hydrogeologic unit, by nonwelded tuffs that appear to act as a barrier to gas transport. In the fractured tuffs of the Topopah Spring welded unit, sampled by borehole USW UZ-1, the ^{14}C content of the gas decreases with depth to 25 pmc. The CO_2 concentrations and ^{13}C signature of the gases are similar to the values observed at UZ-6S. These data are consistent with diffusive transport of $^{14}CO_2$ from the surface in response to radioactive decay of ^{14}C at depth.

384 **QUALITY ASSURANCE FOR RADIOLOGICAL EMERGENCY RESPONSE FIELD LABORATORIES.** **Paul B. Hahn, U.S. Environmental Protection Agency, P.O. Box 93478, Las Vegas, NV 89193**

In the event of a radiological emergency or emergency response exercise, a Federal Radiological Monitoring and Assessment Center (FRMAC) may be established to provide the monitoring and assessment needs of the states for the particular accident. The Center may request the services of mobile analytical laboratories which are maintained by state and federal agencies or their contractors. These facilities would be transported to the accident area to provide radioanalytical support to the Center during the initial emergency and ensuing restoration and reentry phases.

This presentation will describe the mobile analytical support facilities which are generally available to a FRMAC and a proposed quality assurance plan to demonstrate and document the actual capabilities of the responding laboratories. Results of analyses of known samples at FRMAC ' 93 in Omaha will be presented.

385 THE IN-HOUSE CONTINUING EDUCATION PROGRAM FOR TECHNICAL STAFF AT AN ANALYTICAL SERVICES LABORATORY. **James R. Noyce, and Mathias M. Lardy I.T. Analytical Services, 2800 George Washington Way, Richland, Washington 99352.**

The sophistication of radioanalytical operations at analytical services laboratories is increasing while the turn-around times desired by clients are decreasing, and yet quality is expected to improve also. These conditions require both a wider and deeper knowledge by the technical staff of what occurs in the laboratory, from receipt of a request for analysis through preparation of results reports to proper disposition of samples residues and analytical wastes. Regular safety and quality meetings, on-the-job training and cross training, off-site seminars, and reimbursement for education tuitions are necessary but not sufficient. Our laboratory has a two-component program to raise further the proficiency of our technical staff. The first component is a mentoring program for some of the team leaders, chemists, and experienced technicians. The second, more recent component is an on-going series of weekly seminars called the Brown Bag Technical Sessions. These are presented by members of the technical staff, and anyone interested in the current topic may attend.

386 EMERGING ISSUES IN AUTOMATED ENVIRONMENTAL RADIOCHEMISTRY DATA VERIFICATION, VALIDATION, AND ASSESSMENT. **Keith A. Wegner, Steven A. Ziliak, Gregg A. Starkel, David W. Moody, David M. Etzel, QuantaLex, Inc., 300 Union Blvd., Suite 600, Lakewood, CO 80228**

Independent verification, validation, and assessment of radiochemistry data has traditionally been performed manually with data reviewers relying more on calculators than on computers as process tools. Increasingly, some or all of the data verification, validation, and assessment processes are being automated. Computerized algorithms identify and flag data deficiencies, anomalies, and outliers which speeds up the review procedure. Automation tends to make the data review process more efficient on some levels but their effectiveness is heavily dependent on how the automated system is configured at the outset. Systems which can be modified and tailored to fit the site or facility from which the data was obtained will be more effective than" a "hard-wired" system. Environmental radiochemistry data is particularly sensitive to the algorithms used to evaluate MSAs, efficiencies, uncertainties, resolution, chemical recoveries, and so forth. Some aspects of the assessment process, as distinguished from verification and validation are not fully amenable to an algorithmic treatment and must still be evaluated manually. If data is not available from the radiochemical laboratory in the appropriate electronic format, then it must be entered into an automated system manually resulting in diminished returns for overall data review efficiency. These issues and how they are being dealt with in automating environmental radiochemical data evaluation processes will be discussed in this paper.

387 EXPERIENCE WITH PERFORMANCE SPECIFICATIONS FOR SOME RADIOCHEMICAL ANALYSES, **Carl T. Bishop. FERMCO, P.O. Box 398704, Cincinnati, Ohio 45239**

Performance specifications, rather than the use of "Approved Procedures," are being used as criteria in determining the acceptability of Radiochemical analyses being carried out at the Fernald site in Ohio. Performance specifications, relating to minimum detectable concentration, precision, and accuracy in the analysis of standard and spiked samples, have been established for all analytical work associated with the clean-up at Fernald. Experience in the area of uranium and gross alpha and gross beta analysis will be presented.

As a specific example, the performance criterium for the percent recovery in the analysis of a known standard in the determination of total uranium in water by Kinetic Phosphorescence Analysis, is that the recovery be between 75 and 125%, when that standard is analyzed with each batch of samples. Experience in analyzing water samples for uranium, over a four month period, resulted in recoveries ranging from 70 to 108% with an average recovery of 101 %.

388 **The American Society for Testing and Materials (ASTM) was organized in 1898 for the voluntary development of standard methodology. ASTM is a not-for-profit organization that provides a forum for producers, users, consumers and persons having a general interest to meet and write standards for materials, products, systems, and services. ASTM has many committees which cover a large scope of areas and interest. One such committee is D-19 on Water. The scope of this committee is the study of water, the promotion of knowledge thereof, and the standardization of terminology for sampling and analysis of water, surface-water hydraulics, performance of materials used to modify water characteristics, and detennination of the corrosivity or deposit forming properties of water. Subcommittee D 19.04 is charged with the development of standards for determining gross and specific radionuclide concentrations in water and water-formed deposits using chemical and instrumental measurements. This presentation will describe the consensus standard process for writing and testing methods for radionuclide analyses.**

389 **SCREENING FOR SPECIFIC RADIONUCLIDES - A NECESSARY DEVELOPMENT?** Terry McKibbin, 3503 E. Highway 56, Berthoud, Colorado 80513.

For the purpose of handling "significant" levels of radioactivity in laboratory samples, the need for isotope specific radioactive screening data is of inportance for the following reasons: 1) Licensed levels are designated by atonic ranter categories. The isotopes of specific categories can be determined through screening techniques. 2) Allowable (exempt) levels differ according to nuclide. 3) The biohazard varies for different radionuclides. 4) Inventory of radioactive material, necessary for license ccrtpliance, is non-existent using gross counting data. 5) Better field decisions can be made with the isotope specific information. The advantage of isotope specific screening includes acceptability for specific laboratories, sampling decisions, and need for further analyses. Screening capabilities already exist to allow isotopic identification for many important radionuclides. Some enhancements are currently undergoing testing that would increase sensitivities and assist in the positive identification of specific radionuclides. Some of the systems that can assist in this screening process include: 1) Liquid scintillation with alpha/beta descrimination capability. 2) Large area beta detectors. 3) FIDLER - low energy photon detector. 4) Extended range photon spectrometers with gamma and x-ray analytical software. 5) Large area alpha spectrometers. Along with some process knowledge, these screening data can formulate a basis for health physics decisions, sample management, regulation compliance, and inventory for analytical laboratories. This qualitative and quantitative approach to radioactive material screening cannot replace the sensitivities of laboratory analyses, but can serve an important intermediate role in the handling of samples contaminated with higher levels of radioactive material.

390 **RADON-222 IN WATER AT PUBLIC WATER SUPPLY SYSTEM WELLHEADS**

Loren A. Berge. Scientific Laboratory Division - NM-DOH, P.O. Box 4700 Albuquerque, NM 87196-4700.

A New Mexico-wide survey of the occurrence of Radon-222 in ground waters used by public water supply systems was performed Mar-93 through May-94. The survey was a joint project of the NM Department of Health - Scientific Laboratory Division's Radiochemistry Section, and the NM Environment Department's Drinking Water Bureau. Samples were collected as wellhead samples to measure the source water in full recognition that this would be an 'upper case' approach; radon will not be, in general, created once the water is removed from the aquifer, but likely will be lost as water is transported to the household tap. This presentation will report on the concentration distribution observed. Over 650 different wellheads have been measured from over 325 different water supply systems from all regions (20 field offices) of New Mexico. State-wide the results are: over 95% @ > 100 pCi/L; approximately 65% @ >300 pCi/L, the U.S. EPA's SDWA proposed MCL; about 20% @ > 1000. pCi/L; and, the highest @ 7800 pCi/L.

391

Abstract Not Available

392 **THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN VARIOUS MATRICES BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS.**

James R. Budahn, U.S. Geological Survey, Box 25046, MS 973, Denver Federal Center, Denver, Colorado 80025.

Instrumental neutron activation analysis (INAA) is a highly precise, non-destructive analytical technique capable of determining up to 50 elemental concentrations in a wide range of sample matrices. Over the past 15 years, INAA methods have been developed for the analysis of unusual geological and biological materials such as ultramafic rocks, mineral separates, tree and plant materials, whole fish and fish livers. Dependent on the specific matrix selected for analysis by INAA in addition to the element(s) of interest, the irradiation and counting conditions of materials have high concentrations of elements that can generate significant radioactive emission rates, and therefore, the precise analyses of these types of samples require relatively low neutron fluences and generally long decay times. In contrast, in order to obtain very low detection limits in biological materials, very high neutron fluences and short decay times are required. Adjustments in counting parameters are also important in improving the overall precision of INAA.

393 **RADIOSTRONTIUM ANALYSES OF ENVIRONMENTAL MEDIA USING CERENKOV COUNTING.**

D.E. McCurdy, Yankee Atomic Environmental Laboratory, 580 Main Street, Bolton, MA 01740.

The Yankee Atomic Environmental Laboratory has validated several radiochemical procedures for the measurement of radiostrontium in environmental media using Cerenkov radiation counting of the final matrix. The environmental media evaluated thus far include water, vegetation, air particulate filter paper and milk. The radiochemical procedures involve various initial matrix preparation techniques, a single-step chemical purification using an EiChroM Sr Spec column and a final radiometric analysis of ^{90}Sr and ^{90}Y by Cerenkov radiation counting. A flow diagram of the basic technique and limited validation data shall be presented for each media. Typical parameters of the techniques, such as processing time, chemical recovery, sample volume, detection efficiency, detector background and limit of detection, shall be presented.

LOW LEVEL ALPHA DETECTION BY CHEMICAL MEANS, M. P. Neary, NUS Laboratory, 5350 Campbells Run Road, Pittsburgh, PA 15205.*

Normally alpha particle detection depends either on the direct interaction between an active surface such as a silicon barrier detector or on the alpha-gas interaction to create charged gas species thus by either means, altering the electrical conduction to result in an electrical pulse . Both means are considered to be low background methods and as such exhibit low MDAs. The associated instrumentation is both expensive and not well suited for field use. A method is described and the associated instrumentation suggested that vitiates both problems but retaining the low background character. Additionally, the method reported has substantially higher counting efficiencies. It is well known that alpha and beta particles produce ionized species by their interaction with matter. When such particles pass through aqueous solutions certain oxygen centered free radicals are formed. Peroxy and hydroxy free radicals are two such species, both of which are strong oxidizing agents. This report describes these agents, generated by alpha particles, coupled with the magnesium-catalyzed luminol chemiluminescence reaction. Variation in light levels as a function of alpha activity permitted quantitation. The detection means include a simple luminometer for analog measurements and a single channel analyzer for digital measurements.

* This work performed while the author was an employee of Cardinal Associates Inc 1217 Parkway Drive, Santa Fe, NM 87501

395 BUYING RADIOCHEMICAL ANALYSIS SERVICES--HOW *TO* GET THE MOST FOR YOUR MONEY
Marilyn J. Ayers, Keith Wegner, QuantaLex, Inc., 300 Union Blvd. Suite 600, Lakewood, Colorado, 80228-1554

Having your radiochemical samples analyzed and getting results which are suitable for the intended uses of the data can be both challenging and frustrating. There are many laboratories to choose from which offer a myriad of radioanalytical services and types of analyses. There are some straightforward techniques which the purchaser of radioanalytical services can use to navigate the maze of services available to obtain high quality, usable data at a reasonable cost.

Such techniques include: **(1)** A carefully planned sampling and analysis strategy; **(2)** Identifi cation of analytes and isotopes to be analyzed; **(3)** Performance-based testing rather than method-based testing; **(4)** Levels of quality assurance and quality control; **(5)** Documentation to be provided with the results; and **(6)** Evaluation of the quality of the data received.

By clearly identifying, to the extent possible, all of the factors which influence each of the six areas described above, the buyer of the radioanalytical services is in a much better position to negotiate fair and reasonable prices for the analyses and obtain data suitable for its intended use.

428 NUMERICAL ANALYSIS OF CONVOLVED ALPHA SPECTRA, M. P. Neary, NUS Laboratory, 5350 Campbells Run Road, Pittsburgh, PA 15205

In some cases the sample that is counted in alpha spectroscopy is a fluoride precipitate that results from chemical treatment of an aliquot of the raw sample. The raw sample may be a solid or semi-solid that may be leached or totally dissolved. The resulting solution is often high in dissolved solids. Aqueous samples may exhibit the same condition. High dissolved solids occasionally results in a prepared sample whose mass exceeds 200ug, giving rise to alpha spectra that are attenuated, that is overlap Such samples produce data that are usable; and require re-analysis, including re-preparation. In some cases it is sufficient to re-dissolve the fluoride and re-precipitate an aliquot, thus reducing the amount of the original sample represented by the new fluoride precipitate, thus increasing the MDA. Numerical analysis of the attenuated spectral data may yield valid data, thus avoiding a re-preparation and re-analysis of the sample. Two algorithms for numerical analysis of convolved alpha spectral data are compared and evaluated. Both employ statistical means of assessing convergence. One is referred to as factor analysis algorithm and the other the Marquardt-Levenberg algorithm.

429 DIAGNOSIS OF GASTRIC CANCER BY (7-T)TETRACYCLINE. Zhi-Min Li, Lan-Xiang Meng, Dong Chen, Ao Yuang, CIAE, 6-14-6 Dong Da Qiao Lu, Chaoyang District, Beijing 100020, China.

The (7-T)tetracycline has a strong affinity to gastric cancer cells. Its biological half-life of excretation is 14 - 16 hours for normal person. One third of the total activity taken orally is excreted in urine after 6 h. Much less than the normal value of activity is excreted by patient who is suffering from gastric cancer . It could be used for diagnosing gastric cancer by determining activity in urine with beta-liquid scintillation counter. 36 patients with gastric disease including cancer have been diagnosed by this method. The results showed that the method is simple,sesitive and reproducible; Patient has not sufferings; It can be used for diagnosing a early stage carcinoma ventriculi.

196 INTEGRATED SAMPLE AUTOMATION FOR ENVIRONMENTAL, FOOD, AND CHEMICAL TESTING. Mark Cava. Zymark Corporation, Zymark Center, Hopkinton, MA 01748.

Government and industrial laboratories must lower costs, improve consistency for QC, and work to apply value-added performance-based methods. A powerful first step is to apply sample automation technology to standard operating procedures. Implementing any productivity enhancer requires change. To help make change effective, laboratories let their most important assets, their best people, drive sample automation projects. These laboratories achieve growth by automating to obtain excellent QC, lowest cost, and fast turnaround. To be more proactive with implementing performance-based methods, laboratories need a cost-effective plan for meeting QC and regulatory quidelines. The global impact of solid phase extraction is the best example to date. In this case, benefits include, huge savings, QC equivalency, and increased capacity for a variety of methods. Domestically, gaining regulatory support depends on good relationships and a satisfactory QC process. Integrated workstation and system sample automation will be examined. Automation techniques for sample concentration, extraction, cleanup, BOD, TSS, and acid digestion will be discussed. The conclusion will examine the relative impact of automation in terms of throughput, and savings.

ULTRA-LOW-COST EXPLORATORY ROBOTIC CONSTRUCTION SYSTEMS FOR PC'S. Evan Rosen. Advanced Design, Inc., 1101 East Rudasill Road, Tucson, AZ 85718.

Inexpensive exploratory robotic construction systems are now available for PC's. Featuring Erector Set-like flexibility, these systems let even novice users assemble and run custom lab-robot demonstrations on demand. An interactive "teach" mode allows scripting of robots without typing, while a built-in editor lets users rearrange or tweak scripts and then replay them in seconds. For relaxed presentations, the mouse can be used to run single lines, extended script sections, or even entire scripts. Advanced experimenters may choose to override the default values of acceleration and max speed and tune these parameters for a specific demo. Users with programming experience can also augment scripting with traditional languages such as C or Microsoft QuickBasic for sensor reading and decision making intermixed with scripted actions. In concert with other lab equipment, applications such as sample pickup, dispensing, weighing, mixing, heating, presentation for spectroscopic scans, and so on, can be assembled and demonstrated with ease.

398 AN INEXPENSIVE ARTICULATE ARM ROBOT FOR EDUCATION AND ENTRY LEVEL ROBOTIC APPLICATIONS. Charles Brooks, Marcraft, Inc., 100 North Morain Street, Kennewick, WA 99336, Rodnev Stockton. SLR Systems, 3100 George Washington Way, Richland, WA 99352.

The ProArm by Marcraft is an inexpensive entry-level articulated robot designed for the educator who demands student proof demonstration and experimental equipment. The arm is capable of a positional accuracy of 0.035 of an inch and a load capacity of 1.1 pounds.

The robot is powered by stepper motors with open loop feedback. Although this precludes the use of this arm for sophisticated applications, with the proper design simple laboratory applications may be performed.

A video of the system as well as an actual demonstration will be shown.

399 COMPARISON OF SOME CURRENTLY AVAILABLE LABORATORY SCALE ROBOTS. Rodnev Stockton. SLR Systems, 3100 George Washington Way, Richland, WA 99352.

A brief overview of various laboratory scale robots will be presented. This will include video as well as handouts. The performance specifications from the various manufacturers will be presented in a tabulated format to allow a better understanding of the current state of the art in laboratory robots.

400 ROBOTIC/LIMS INTERFACE TO A COMBUSTION FURNACE USED IN CONJUNCTION WITH A CARBON/SULFUR ANALYZER. Philip J. Farrellv. President, Hudson Control Group, Inc., 44 Commerce Street, Springfield, NJ 07081, 201-376-7400, Fax 201-376-8265

The design and development of a robotic system to service a Leco RL-700 furnace and carbon/sulfur analyzer will be described. The system automatically identifies each sample via a barcode label, weighs out precise amounts of powdered sample into ceramic crucibles, adds accelerator powders, then loads the crucibles into the furnace. The robot's host computer operates the furnace, collects the results, then transports them to a plant-wide LIMS via a Token Ring network. The self-prompting menus and simplified operation of the system allow round-the-clock usage of the system even by lightly-trained technicians.

401 VALIDATING A BLOOD GLUCOSE DATA ACQUISITION SYSTEM IN TODAY'S FDA ENVIRONMENT. Aimee Scheiman. LifeScan Inc., a Johnson & Johnson company, 1000 Gibraltar Drive, Milpitas, California 95035. Scott Atkin, Sagian, Inc., 5835 West 57th Street, Indianapolis, Indiana 46278

A case study of validating a blood glucose data acquisition system will be presented from the end-user's and the software/hardware vendor's perspective. The specter of FDA requirements is challenging, but actually make good business sense. The lessons we have learned and the lessons we wish we did not have to learn will be discussed. These lessons will be applied to the next automation project. From the end-user's perspective, key lessons were learned in the areas of: project planning, capital appropriation planning, feature creep, and managing demands from many departments. By focusing on the actual internal requirements, that reflect the FDA's expectations, the validation process began to make progress. From the software/hardware vendor's perspective, key lessons were learned in the areas of: project management, bidding, change orders, hardware selection, quality procedures, source code version control, customer support during validation, bug fixing, and feature creep. The process of validating a complex system must start at the very beginning of the project. Internal and FDA requirements are numerous and time consuming. A good understanding of the objectives and requirements before starting the project will enable one to validate an automated system successfully.

402 VERIFICATION SYSTEM FOR AN AUTOMATED SCREW-CAP REMOVAL DEVICE. Gerald L. Hoffman. U.S. Geological Survey, National Water Quality Laboratory, Methods Research and Development Program, 5293 Ward Road, Arvada, Colorado 80002.

Automated procedures, which require removal of screw caps from bottles, need a verification system to determine when caps do not come off or go on successfully. A method to determine when a cap has been removed or replaced was devised using a commercially available infrared-photorelay sensor (IPRS). The IPRS used was originally designed as an indoor security alarm system. During operation, a directional infrared (IR) beam (originating from the IPRS unit) is bounced off a reflector target back to the IPRS sensor. When the IR beam is blocked, a normally open switch in the IPRS unit is closed electronically. For this application, the IPRS unit was mounted below a bottle uncapping/capping device (BUCD). The BUCD was modified by applying a small circle of reflective tape to the bottom of the unit perpendicular to the screw-cap-gripper fingers. A cap removed from a bottle and retained in the gripper fingers will effectively stop the IR beam from reflecting back to the sensor in the IPRS unit. When the IR signal is blocked, the resulting closed-switch position can be monitored with a programmable event controller, which is connected to a computer through a RS232-C interface. If the BUCD is unsuccessful in removing the cap from a bottle, the IR beam will be reflected back to the IPRS unit, causing an open switch position. By monitoring the IPRS switch status, the cap-removal process can be verified and automatically incorporated into the robotic system software, which can be programmed to take corrective action. For example, if a cap is not removed from a bottle after three attempts, the bottle can be rejected and a message printed to the operator for corrective action.

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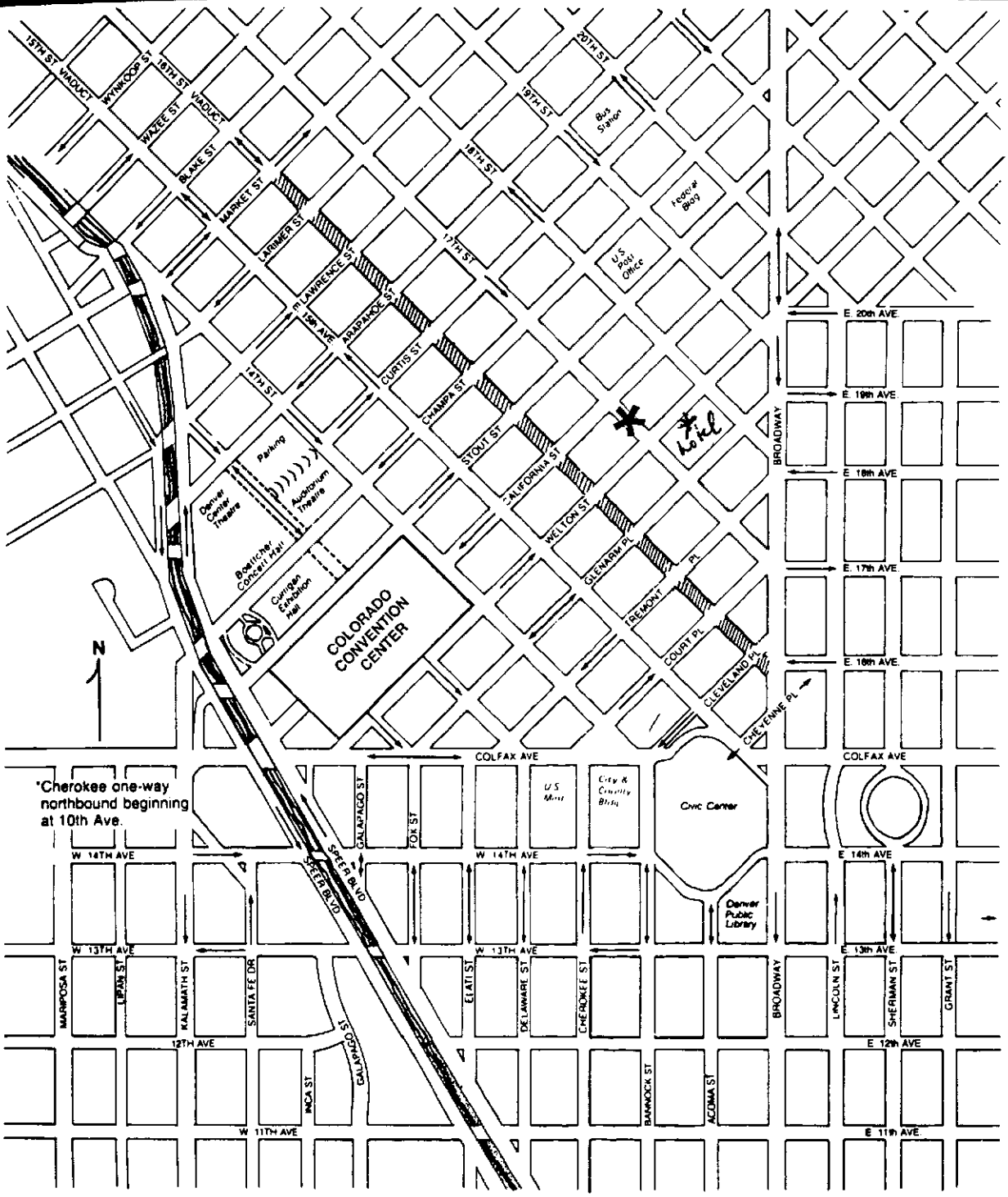
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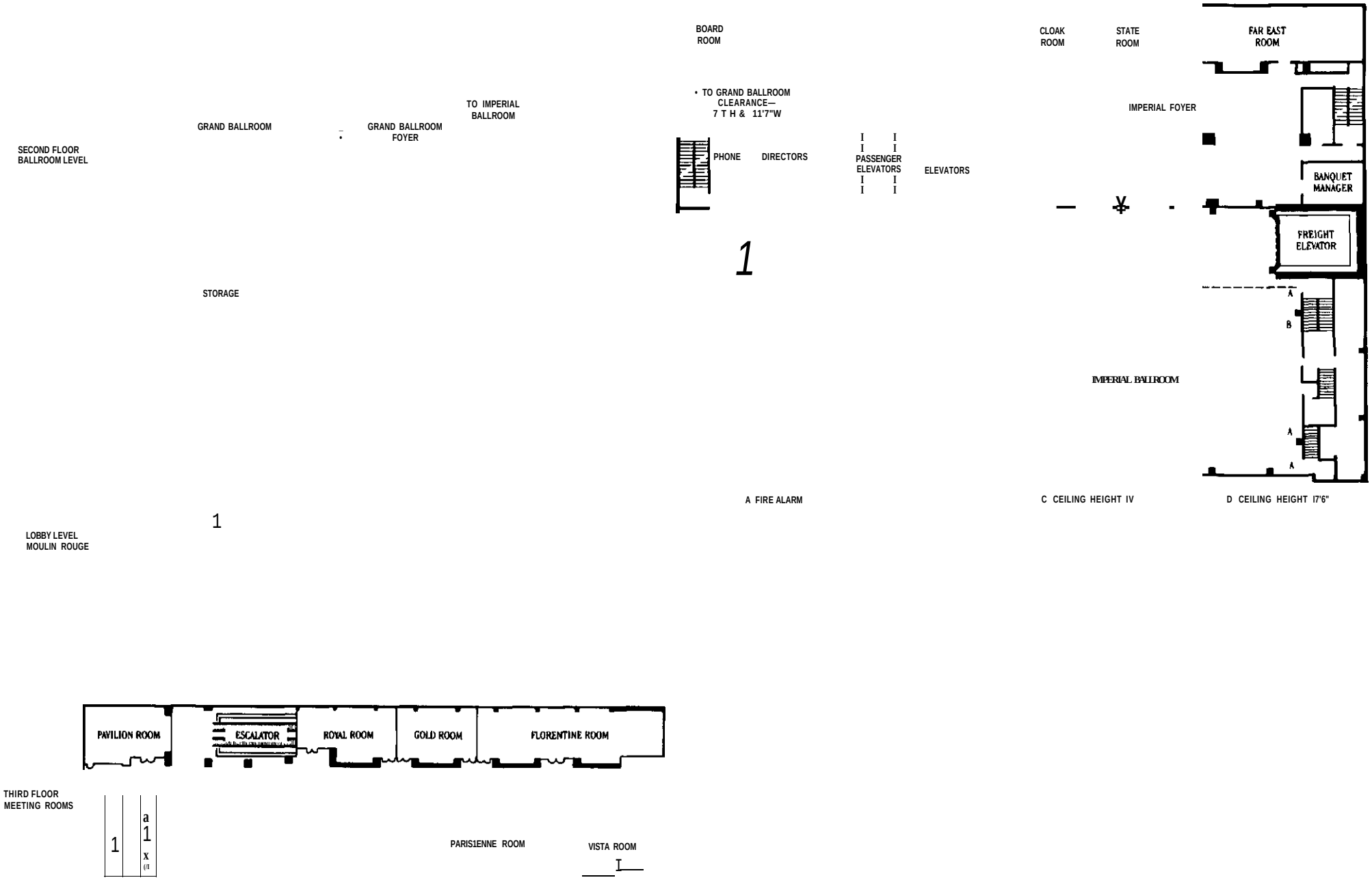
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STORAGE
1
LOBBY LEVEL
MOULIN ROUGE
BOARD
ROOM
• TO GRAND BALLROOM
CLEARANCE—
7 T H & 11'7"W
PHONE
DIRECTORS
PASSENGER
ELEVATORS
ELEVATORS
1
A FIRE ALARM
CLOAK
ROOM
STATE
ROOM
FAR EAST
ROOM
IMPERIAL FOYER
BANQUET
MANAGER
FREIGHT
ELEVATOR
A
B
IMPERIAL BALLROOM
A
A
C CEILING HEIGHT IV
D CEILING HEIGHT I7'6"
PAVILION ROOM
ESCALATOR
ROYAL ROOM
GOLD ROOM
FLORENTINE ROOM
THIRD FLOOR
MEETING ROOMS
1
a
1
x
PARIS1ENNE ROOM
VISTA ROOM